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(51) International Patent Classification <sup>6</sup> : <b>C11D 3/39, C07D 257/02, 257/10, D21C 9/16</b>		A2	(11) International Publication Number: <b>WO 98/03626</b>
			(43) International Publication Date: 29 January 1998 (29.01.98)
(21) International Application Number: PCT/US97/12744		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 22 July 1997 (22.07.97)			
(30) Priority Data: 08/684,670 22 July 1996 (22.07.96) US 08/804,776 24 February 1997 (24.02.97) US			
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(54) Title: METAL LIGAND CONTAINING BLEACHING COMPOSITIONS

(57) Abstract

The invention provides a novel composition for bleaching cellulose based materials, such as wood pulp and paper which includes using an effective amount of a source of an oxidant and an oxidatively stable bleach activator having structure (I) wherein Y<sub>1</sub>, Y<sub>3</sub> and Y<sub>4</sub> each represents a bridging group having zero, one, two or three carbon containing nodes for substitution, and Y<sub>2</sub> is a bridging group having at least one carbon containing node for substitution. Each node contains a C(R), C(R<sub>1</sub>)(R<sub>2</sub>), or a C(R)<sub>2</sub> unit. Each R may be H, alkyl, cycloalkyl, cycloalkenyl, alkenyl, aryl, alkynyl, alkylaryl, halogen, alkoxy, or phenoxy, CH<sub>2</sub>CF<sub>3</sub>, CF<sub>3</sub> and combinations thereof, or form a substituted or unsubstituted benzene ring, or together with a paired R substituent bound to the same carbon atom form a cycloalkyl or cycloalkenyl ring; M is a transition metal; Q is any counterion; and L is any labile ligand.

Reaction conditions:

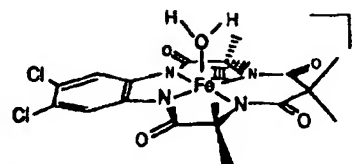
Catalyst: [Fe(DCB\*) (H<sub>2</sub>O)]<sup>-</sup>

Oxidant: 5000 equiv. H<sub>2</sub>O<sub>2</sub>

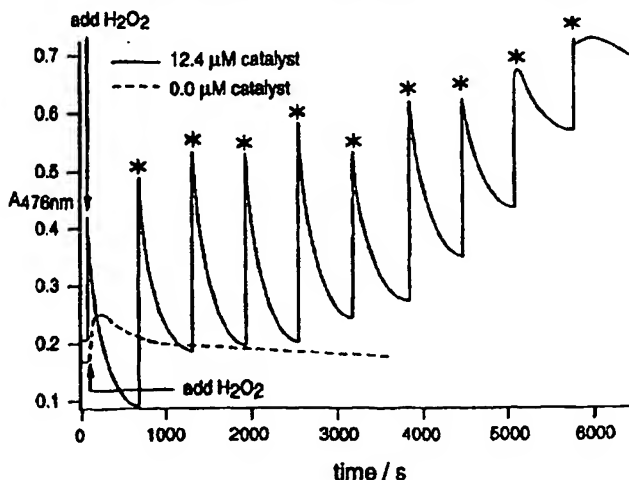
T: 25°C

pH: 10(0.1 M Na<sub>2</sub>CO<sub>3</sub>/NaHCO<sub>3</sub>)

Sequesterant: Dequest 2066



\* = add 60 µL of saturated solution of alkali lignin and H<sub>2</sub>O<sub>2</sub> (5000 equiv)



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## TITLE: METAL LIGAND CONTAINING BLEACHING COMPOSITIONS

5 This work was supported by the National Science Foundation, grant CHE9319505, and the National Institute of Health, grant GM-44867.

BACKGROUND OF THE INVENTIONField of the Invention

10 The invention relates to the use of macrocyclic metal ligand complexes as bleaching catalysts, and more particularly, to transition metal complexes of macrocyclic tetraamide ligands as catalysts for enhancing oxidative bleaching reactions.

15 Brief Description of the Background of the Invention

The United States and Canada are the world's leading producers of wood pulp used for the production of paper and paper board. In 1983, the United States produced over 41 million metric tons of pulp, 39% of the world capacity. The worldwide level of production has been increasing dramatically since then. Pulp, which is made either mechanically or chemically from wood, contains 1) cellulose, a linear polymer of d-glucose of the formula  $-(C_6H_{10}O_5)-$ ; 2) lignin, an amorphous nonuniform three dimensional molecule having the following general composition,  $C_9H_{8.83}O_{2.37}(OCH_3)_{0.96}$ ; and 3) extractives, components of the wood pulp which are typically extracted prior to use of the pulp in a paper making process. See generally, W.G. Glasser and S. Sarkanen, eds. "LIGNIN PROPERTIES AND MATERIALS," American Chemical Society Symposium, Series 397.

30 Desirable qualities for paper include strength, whiteness and brightness. The strength of the paper is related to the viscosity of the pulp

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employed in its manufacture which, in turn, is related to the condition of the cellulose after the pulping operation. Molecular cellulose, as explained above, is a linear chain of d-glucose which naturally forms long  
5 fibers. The longer the individual cellulose fibers, the higher the viscosity of the pulp, and in turn, the greater the strength of the paper. Thus, during processing, it is most desirable to avoid cleaving the cellulose polymers into smaller units.

10           Whiteness is based on the appearance of the paper to observers and its measure is therefore subjective. Brightness is a measure of reflected light at 475nm. The more incident light that is reflected, rather than absorbed, the brighter the paper.

15           Brightness is obtained by bleaching. Pulp bleaching is defined as the treatment of cellulose fibers with chemicals to increase brightness. Bleaching chemicals increase brightness by removing and decolorizing the lignin in the pulp. Lignin exhibits a  
20 yellowish to a deep brown color, depending on the type of wood.

          The most common bleaching chemicals are the oxidants chlorine, hypochlorite and chlorine dioxide. Oxygen gas in conjunction with NaOH may also be used,  
25 but requires expensive equipment and must be used in large amounts. Oxygen also results in loss of pulp strength resulting from free radical damage to the cellulose polymers.

30           Chlorine and hypochlorite can result in loss of strength if used improperly, but in general are effective and easy to use oxidants. Chlorine dioxide achieves a high level of brightness without pulp degradation. However, the chlorine based oxidants all produce as effluent chlorinated byproducts that are

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hazardous to the environment and to health. In addition, chlorine, for example, can react violently with combustible materials. It reacts with  $H_2S$ ,  $CO$  and  $SO_2$  to form toxic and corrosive gases; and, in liquid form, causes burns, blistering and tissue destruction. In gaseous form, it causes severe irritation to eyes, nasal passages and respiratory tissue. In high doses, it can be lethal.

Chlorine dioxide bleach decomposes into  $Cl_2$ , which is toxic and corrosive.

Notwithstanding the hazards to the environment, the chlorine-based oxidants are the most widely used for pulp bleaching in the United States. Commercial pulp and paper bleaching facilities actually uses a combination of several methods. One widely used bleaching sequence begins with chlorination, followed by extraction with  $NaOH$ , treatment with chlorine dioxide, more  $NaOH$  extraction and then more chlorine dioxide treatment. A modification of that sequence adds a hypochlorite oxidation step between the first  $NaOH$  extraction and first treatment with chlorine dioxide. In another sequence, the second  $NaOH$  extraction and second chlorine dioxide treatment are eliminated.

An alternative to the chlorine based oxidants for bleaching is hydrogen peroxide.  $H_2O_2$  oxidizes and brightens lignin and produces high yields of pulp. It is easy to use and does not require expensive equipment. In use,  $H_2O_2$  dissociates to produce the perhydroxyl ion,  $OOH^-$ , which decolorizes lignin and does not attack cellulose. However, if  $H_2O_2$  decomposes, it produces free radicals of oxygen,  $\cdot O_2^-$ , and hydroxide,  $\cdot OH$ , which fragment the lignin and degrade the cellulose. While hydrogen peroxide itself is a

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strong oxidant which can burn skin and mucous membranes, it is not a serious hazard in low (<8%) concentrations and its use does not introduce elemental toxicity into the environment. The major drawback to use of  $H_2O_2$  as the oxidant for pulp and paper bleaching is that it is very slow and expensive to use. Although  $H_2O_2$  would clearly be preferred for its environmentally friendly characteristics, the slow bleaching rate and the high cost associated with its use contribute to reducing its commercial desirability. When used commercially, it is as an adjunct to chlorination and/or chlorine dioxide bleaching or to bleach the effluent.

Certain transition metal chelates have been researched for unrelated purposes. For example, complexes of high oxidation state transition metals are known to function as oxidants in numerous biological reactions under the influence of a protein matrix and in recent years a widespread interest in understanding the mechanism of action and the reactivity of certain monooxygenase catalysts has developed.

An exemplary program is described in Collins, T.J., "Designing Ligands for Oxidizing Complexes," *Accounts of Chemical Research*, 279, Vol. 27, No. 9 (1994). This article lays out a design oriented approach for obtaining ligands that are resistant to oxidative degradation when coordinated to highly oxidizing metal centers. Several diamido-N-diphenoxido and diamido-N-alkoxido acyclic chelate compounds and macrocyclic tetraamido-N chelate compounds are described in the Collins *Accounts of Chemical Research* article.

An azide based synthetic route to macrocyclic tetraamido ligands is described in Uffelman, E.S.,

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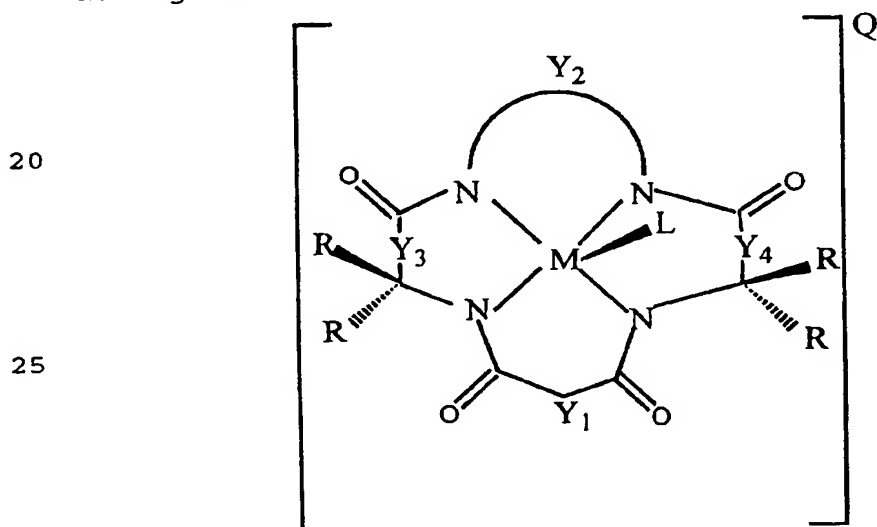
Ph.D. Thesis, California Institute of Technology, (1992). Additionally, synthesis of an aryl bridged tetraamido ligand via the azide based route can proceed by using an aromatic diamine as a starting material.

5 However, the art has not recognized that certain macrocyclic tetraamido ligands will provide novel and unusually effective bleach activators for peroxy compounds. Additionally, it has not been taught, disclosed or suggested that these types of  
10 compounds will be unusually advantageous in the areas of pulp and paper bleaching.

#### SUMMARY OF THE INVENTION

The invention comprises a bleaching composition comprising:

15 (a) an oxidatively stable bleach activator having the structure



30 wherein  $Y_1$ ,  $Y_3$  and  $Y_4$  each represents a bridging group, having zero, one, two or three carbon containing nodes for substitution, and  $Y_2$  is a bridging group having at least one carbon containing node for substitution, each said node containing a  $C(R)$ ,  $C(R_1)(R_2)$ , or a  $C(R)_2$  unit

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and each R substituent is the same or different from the remaining R substituents and is selected from the group consisting of H, alkyl, cycloalkyl, cycloalkenyl, alkenyl, aryl, alkynyl, alkylaryl, halogen, alkoxy, or phenoxy,  $\text{CCH}_2\text{CF}_3$ ,  $\text{CF}_3$ , and combinations thereof, or form a substituted or unsubstituted benzene ring of which two carbon atoms in the ring form nodes in the Y unit, or together with a paired R substituent bound to the same carbon atom form a cycloalkyl ring, which may include an atom other than carbon, e.g., cyclopentyl or a cyclohexyl ring; M is a transition metal with oxidation states of I, II, III, IV, V, VI, VII or VIII or selected from Groups 6, 7, 8, 9, 10 and 11 of the Periodic Table of the Elements; Q is any counterion which would balance the charge of the compound on a stoichiometric basis; L is any labile ligand; and

(b) an effective amount of a source of an oxidant.

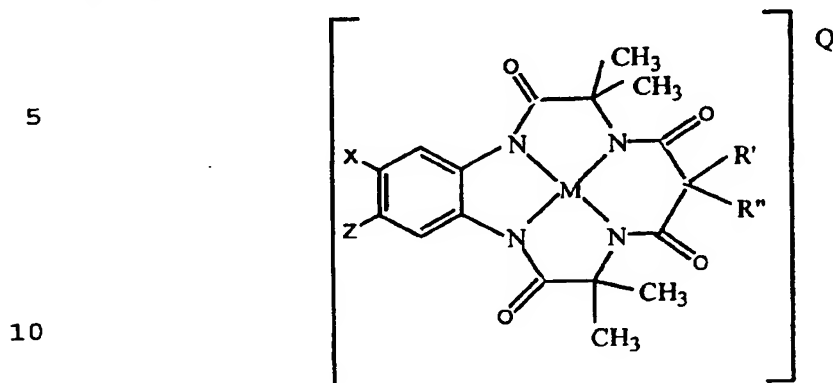
Sequesterants, stabilizers and other standard pulp and paper bleaching adjuncts well known to those skilled in the art of pulp and paper bleaching may be added.

The preferred bleach activators are macrocyclic tetraamido compounds. Of these, those having a substituted aromatic substituent fused directly into the ligand's cyclic structure are especially preferred.



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For example, a preferred compound has the structure:



wherein X and Z may be H, electron donating or electron-withdrawing groups and R' and R'' may be any combination of H, alkyl, cycloalkyl, cycloalkenyl, alkenyl, aryl, alkynyl, alkylaryl, halogen, alkoxy, or phenoxy substituents, or combine to form a cycloalkyl or cycloalkenyl ring, which may contain at least one atom that is not carbon; M is a transition metal with oxidation states of I, II, III, IV, V, VI, VII or VIII or selected from Groups 6, 7, 8, 9, 10 and 11 of the Periodic Table of the Elements; Q is any counterion which would balance the charge of the compound on a stoichiometric basis.

The rapid growth in the pulp and paper industry and the increasing reliance on chemical bleaching processes to provide bright, strong paper products necessarily increases the release of chlorinated byproducts into the environment. The industry needs a safer alternative to chlorine based oxidants for bleaching. Thus, there is a need for a method for bleaching pulp which significantly reduces the discharge of toxic substances into the environment. There is a further need for an environmentally nontoxic

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method which is easy to use and which will produce bright, strong paper.

The catalyst activator of the present invention has been determined to be particularly well-suited to handle this task. The activator has been shown to rapidly increase the rate of alkali lignin bleaching upon the addition of hydrogen peroxide. Furthermore, the activator of the present invention has been shown to be very stable.

There is a need for a novel bleach activator which has sustained catalytic stability in a buffered solution.

There is a further need for a novel bleach activator which can be used in substoichiometric amounts relative to the oxidant compound.

The present invention provides a method of bleaching pulp, paper and other cellulose-based materials comprising generally, the steps of contacting such materials, in stream or batch form, with a source of an oxidant, preferably a peroxy compound, and more preferably hydrogen peroxide and/or its dissociation products, and catalytic, or substoichiometric, amounts of the bleaching activator of the composition described above. The method preferably further includes the addition of a sequesterant for shielding the peroxy compound from exposure to trace amounts of metal which can decompose it unnecessarily.

The method may be run at a variety of temperatures, but preferably within the range of ambient to 80°C, and more preferably between ambient to 40°C. Temperature, however, does not appear to be critical. A wide range of temperatures are suitable.

The preferred pH range is between 7 and 11, and preferably between 9 and 11.

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While the activator of the present invention has been shown in other applications to be an excellent activator of oxidation reactions in solution in general, and particularly as an activator for  
5 activating strong O-atom transfer oxidants, such as hydrogen peroxide, t-butyl hydroperoxide, cumyl hydroperoxide, hypochlorite and peracids, the preferred use in the method of the present invention is as an  
10 activator of peroxy compounds, and most preferably as an activator of hydrogen peroxide in pulp and paper bleaching. The composition of the present invention enhances the oxidative capabilities of hydrogen peroxide thereby greatly enhancing the commercial utility of this environmentally friendly oxidant.

15 The benefits to the environment can not be overstated. Thousands upon thousands of metric tons of environmentally undesirable and even highly toxic, mutagenic or carcinogenic byproducts no longer need to be generated. The method of the present invention can  
20 significantly reduce, if not replace the use of chlorine-based bleaching oxidants and the toxic byproducts their use generates.

#### BRIEF DESCRIPTION OF THE DRAWINGS

25 Fig. 1 is a graph showing the sustained activating stability of the preferred compound of the present invention when added with hydrogen peroxide to a sample of lignin as compared to a control using hydrogen peroxide alone.

30 Fig. 2 represents the UV/Visual absorption spectrum of alkali lignin.

Fig. 3 depicts a synthetic route for preparing the macrocyclic tetraamido ligands of the invention via the azide route.

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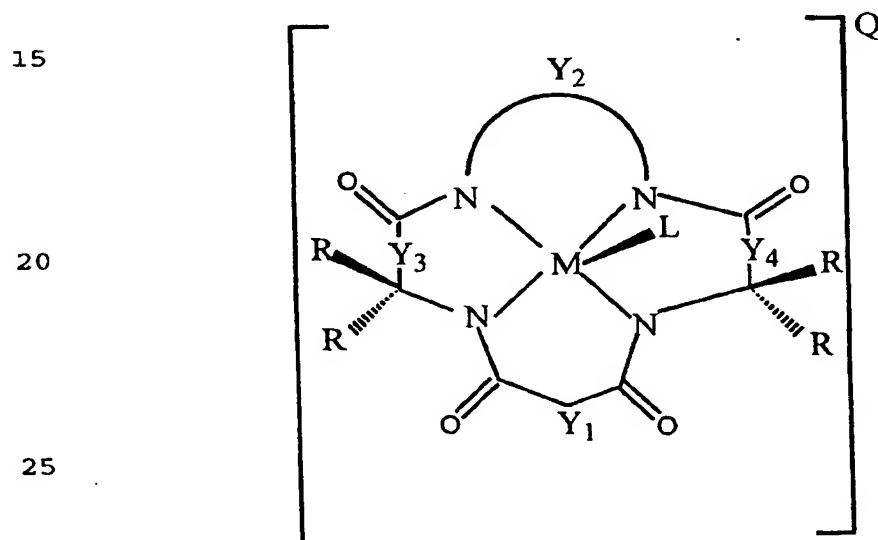
Fig. 4 depicts a synthetic route for preparing the macrocyclic tetraamido ligands of the invention via the azide route using an aromatic diamine as a starting material.

5 Fig. 5 is a graph comparing the sustained catalyst stability of preferred embodiments of the invention versus control.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The invention comprises a bleaching  
10 composition comprising:

(a) an oxidatively stable bleach activator having the structure



wherein  $Y_1$ ,  $Y_2$ , and  $Y_4$  each represents a bridging group having zero, one, two or three carbon containing nodes for substitution, and  $Y_2$  is a bridging group having at least one carbon containing node for substitution, each said node containing a  $C(R)$ ,  $C(R_1)(R_2)$ , or a  $C(R)_2$  unit and each R substituent is the same or different from the remaining R substituents and is selected from the

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group consisting of H, alkyl, cycloalkyl, cycloalkenyl, alkenyl, aryl, alkynyl, alkylaryl, halogen, alkoxy, or phenoxy,  $\text{CH}_2\text{CF}_3$ ,  $\text{CF}_3$ , and combinations thereof, or form a substituted or unsubstituted benzene ring of which two carbon atoms in the ring form nodes in the Y unit, or together with a paired R substituent bound to the same carbon atom form a cycloalkyl or cycloalkenyl ring, which may include an atom other than carbon, e.g., cyclopentyl or a cyclohexyl ring; M is a transition metal with oxidation states of I, II, III, IV, V, VI, VII or VIII or selected from Groups 6, 7, 8, 9, 10 and 11 of the Periodic Table of the Elements; Q is any counterion which would balance the charge of the compound on a stoichiometric basis; L is optionally present and may be any labile ligand; and

(b) an effective amount of a source of an oxidant.

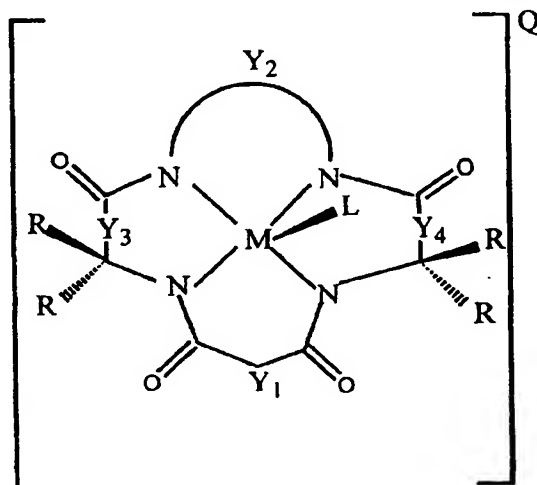
Of these, the preferred inventive macrocyclic tetraamido ligands have proven to be surprisingly effective in a diverse group of performance characteristics for bleach activators.

These ligands are prepared in accordance with the procedures shown in Figs. 3 or 4, and include the preferred embodiments of the ligands set forth in detail in United States patent application of Collins et al., entitled LONG-LIVED HOMOGENOUS OXIDATION CATALYSTS, Serial No. 08/681,237, filed July 22, 1996, which is incorporated herein by reference.

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1. The Macrocyclic Tetraamido Ligands

The inventive compounds have the structure:

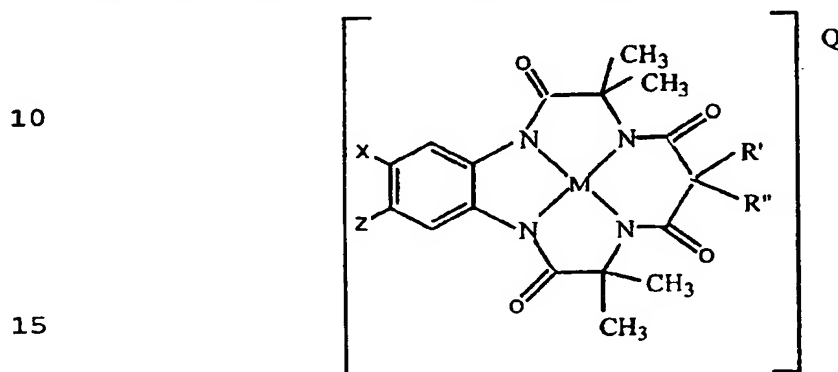


wherein  $Y_1$ ,  $Y_3$  and  $Y_4$  each represents a bridging group having zero, one, two or three carbon containing nodes for substitution, and  $Y_2$  is a bridging group of at least one carbon containing node for substitution, each said node containing node a  $C(R)$ ,  $C(R_1)(R_2)$ , or a  $C(R_2)$  unit and each R substituent is the same or different from the remaining R substituents and is selected from the group consisting of H, alkyl, cycloalkyl, cycloalkenyl, alkenyl, aryl, alkynyl, alkylaryl, halogen, alkoxy, or phenoxy,  $CH_2CF_3$ ,  $CF_3$  and combinations thereof, or form a substituted or unsubstituted benzene ring of which two carbon atoms in the ring form nodes in the Y unit, or together with a paired R substituent bound to the same carbon atom form a cycloalkyl or cycloalkenyl ring, which may include an atom other than carbon, e.g., cyclopentyl or cyclohexyl ring; M is a transition metal with oxidation states of I, II, III, IV, V, VI, VII or

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VIII or selected from Groups 6, 7, 8, 9, 10 and 11 of the Periodic Table of the Elements; Q is any counterion which would balance the charge of the compound on a stoichiometric basis; L is any labile ligand.

- 5 An especially preferred embodiment of these inventive compounds is represented by the structure of the macrocyclic tetraamido compounds:



- wherein X and Z may be H, electron donating or electron-withdrawing groups and R' and R'' may be any combination of H, alkyl, cycloalkyl, cycloalkenyl, alkenyl, aryl, alkynyl, alkylaryl, halogen, alkoxy, or phenoxy substituents, or combine to form a cycloalkyl or cycloalkenyl ring, which may contain at least one atom that is not carbon: M is a transition metal with oxidation states of I, II, III, IV, V, VI, VII or VIII or selected from Groups 6, 7, 8, 9, 10 and 11 of the Periodic Table of the Elements; Q is any counterion which would balance the charge of the compound on a stoichiometric basis.

- The X and Z groups can be H, or either electron donors or electron withdrawing groups. Electron withdrawing groups include halogens, such as Br, I and most preferably, Cl<sup>-</sup>. Further, SO<sub>3</sub><sup>-</sup>, OSO<sub>3</sub><sup>-</sup>, OSO<sub>3</sub>R (R being defined, without limitation, as H, alkyl, aryl, alkylaryl) and NO<sub>2</sub><sup>-</sup> are appropriate groups.

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Electron donor groups include alkoxy (without limitation, methoxy, ethoxy, propoxy and butoxy), alkyl (without limitation, methyl, ethyl, propyl, n-butyl and t-butyl) and hydrogen. These groups change the  
5 electron density of the metal ligand complex and impact its reactivity.

R' and R" appear to have an impact on the sustained catalytic stability of the inventive macrocyclic tetraamido ligands. Although each can be  
10 individually chosen from H, alkyl, alkenyl, aryl, alkynyl, halogen, alkoxy, or phenoxy substituents, short chain alkyl appears preferred. Especially preferred is when R' and R" are the same and are selected from ethyl and methyl, or when R' and R"  
15 combine to form a cycloalkyl or cycloalkenyl ring, especially cyclopentyl or cyclohexyl. The cycloalkyl ring may include at least one other atom other than carbon, such as, without limitation, N, O, or S. The most preferred and most robust embodiments are those in  
20 which R' and R" are the same and are selected from the group consisting of methyl, CF<sub>3</sub>, hydrogen, halogen and a five membered ring formed together with the carbon atom to which both are bound. These latter groups are either unreactive, form strong bonds with the cyclic  
25 carbon, are sterically hindered, and/or are conformationally hindered such that intramolecular oxidative degradation is restricted.

The metal M is a transition metal with oxidation states of I, II, III, IV, V, VI, VII or VIII;  
30 or may be selected from Groups 6 (Cr, Mo, W), 7 (Mn, Tc, Re), 8 (Fe, Ru, Os), 9 (Co, Rh, Ir), 10 (Ni, Pd, Pt) and 11 (Cu, Ag, Au). It is preferably selected from the group consisting of Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn (Group 12), Mo and W.



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Q is any counterion which would balance the charge of the compound on a stoichiometric basis. Both negative and positive counterions may be useful. A generally positively charged counterion is preferably chosen from, but not limited to: alkali metal counterions (e.g., K, Li, Na),  $\text{NR}^+$ , and  $\text{PR}^+$ , wherein each  $\text{R}^+$  is individually selected from H, alkyl, aryl, alkylaryl, alkenyl, or can fuse together to form a cycloalkyl or cycloalkenyl or aryl ring which may contain at least one atom other than carbon. A generally negatively charged counterion is preferably chosen from, but not limited to  $\text{BF}_4^-$  and  $\text{PF}_6^-$ .

L is any labile ligand which can attach to M. These include, preferably, but without limitations,  $\text{H}_2\text{O}$ , Cl, and  $\text{C}\equiv\text{N}$ .

Because of the complex nature of these compounds, within the specification, they are not named, but for convenience are referred to by the substituents present in them. The structure represented above, for example, can be titled 5,6(4,5-Di-X-Benzo)-3,8,11,13-tetraoxo-2,2,9,9-tetramethyl-12,12-diethyl-1,4,7,10-tetraazacyclotridecane (or Tetramethyl diethyl di-X-benzene (TMDE-DXB, where  $\text{X} = \text{Cl}, \text{H}, \text{Me}, \text{OMe}$ )). Thus, for convenience, in the above structure, where there are two methyl groups each on the amine members of the ligand, and there are two ethyl groups acting as  $\text{R}'$  and  $\text{R}''$ , the compound is referred to as TMDE. When  $\text{R}'$  and  $\text{R}''$  are methyl groups, the compound is referred to as TMDM. When the groups X and Z are both chloro, the compound is referred to as DCB. The preferred transition metal of the ligand is iron, so the compound can be referred to as Fe-DCB.

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The conventional hydrogen peroxide bleaching methods are practiced at a pH within the range of 11 to 9 and at temperatures within the range of 30 to 80°C, and most often at 50 to 70°C. See, Charles, J.E. et al., 1980 TAPPI Pulping Conference Proceedings, TAPPI Press (1980). When the activator of the present invention is used, the temperature of the reaction can be reduced to ambient temperature. While the catalyst activator can be used at the higher conventional reaction temperatures, it also works well at 35 and 40°C. It is known that, for about every ten degrees in temperature, the reaction rate changes by a factor of about two. Thus, the reaction rate is much faster at higher temperatures. However, when bleaching pulp with the activator of the present invention, rates of H<sub>2</sub>O<sub>2</sub> oxidation which are significantly better than those heretofore possible can be obtained with temperatures much lower than heretofore possible, thereby saving energy costs and increasing plant throughput rates. Preferred temperature ranges are therefore between ambient and 80°C, preferably between ambient and 70°C and most preferably between ambient and 40°C. The bleaching system of the invention will even function effectively at sub-ambient temperatures. The wide range of temperatures over which the catalyst activator will function permits the method of the present invention to be used in existing facilities and in conjunction with other pulp and paper bleaching processes without having to make special temperature adjustments for the peroxide bleaching portion of a commercial production line, other than the advantageous change of lowering the temperature.

The pH of the oxidation reaction can also be lowered when using the activator of the present

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invention. Bleaching experiments run at pH 7 with  $H_2O_2$  and the catalyst activator of the present invention bleached lignin at a rate believed to be an improvement over the conventional  $H_2O_2$  bleaching rate, but not at the best rate possible for the activator. Far more rapid and satisfactory rates were obtained using the pH 10. Thus, the conventional pH range of 11 to 9 need not be altered by the addition of the catalyst activator of the invention, but can be if needed to avoid the decomposition of  $H_2O_2$  that is known to occur at high pH. Decomposition can also be attributed to the presence of trace metals in the bleaching solution with the peroxy compound. Sequesterants and other known stabilizers are used to reduce the likelihood of decomposition due to the presence of trace metals. The experiments set forth below demonstrate that sequesterants may also be used with the catalyst activator of the present invention.

It is further believed that bleaching by the method of the present invention will produce very favorable kappa numbers, a measure used in the pulp and paper industry to show the amount of residual lignin following bleaching. The kappa number, which should be as low as possible, is a ratio of the difference between (1) the total oxidizing equivalent necessary for 100% lignin removal and (2) the difference between the actual oxidation achieved and the total oxidizing equivalent. It is obtained by testing with potassium permanganate according to procedures well known in the pulp and paper industry.

As the inventive macrocyclic tetraamido ligands are true catalysts, or catalyst activators, the amount thereof added to the bleaching compositions is generally substoichiometric. However, it is preferred,

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without limitation, to add about 0.0001 to about 999,999 parts per million (ppm), more preferably 0.001 to 100,000 ppm, to the compositions of the invention.

In the Experimental Section below, selected syntheses of the preferred macrocyclic tetraamido compounds are depicted. Additionally, tests were conducted to demonstrate the lignin bleaching capability and the sustained catalytic activity of these inventive macrocyclic ligands.

## 2. Oxidant Compounds

The oxidant compounds, such as O transfer atoms, preferably peroxy compounds, can be an organic or inorganic compound containing the -O-O-peroxide linkage. Exemplary compounds include hydrogen peroxide, hydrogen peroxide adducts, compounds capable of producing hydrogen peroxide in aqueous solution, organic peroxides, persulfates, perphosphates, and persilicates. Hydrogen peroxide adducts include alkali metal (e.g., sodium, lithium, potassium) carbonate peroxyhydrate and urea peroxide. Compounds capable of producing hydrogen peroxide in aqueous solution include alkali metal (sodium, potassium, lithium) perborate (mono-and tetrahydrate). The perborates are commercially available from such sources as Akzo N.V., and FMC Corporation. Alternatively, an alcohol oxidase enzyme and its appropriate alcohol substrate can be used as a hydrogen peroxide source. Organic peroxides include, without limitation, benzoyl and cumene hydroperoxides. Persulfates include potassium peroxymonosulfate (sold as Oxone®, E.I. duPont de Nemours) and Caro's acid.

An effective amount of peroxy compound is an amount sufficient to generate at least 0.001 ppm active oxygen (A.O.). While not limited thereto, it is

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preferred to produce from about 0.001 to about 1,000 ppm A.O. For fabric bleaching, from about 0.01 to about 50 ppm A.O. is preferred. A description of, and explanation of A.O. measurement is found in the article of Sheldon N. Lewis, "Peracid and Peroxide Oxidations," In: Oxidation, 1969, pp. 213-258, which is incorporated herein by reference.

### 3. Adjuncts

The inventive macrocyclic tetraamido ligands, where desired, can be combined with an adjunct or base, said base comprising: builders and surfactants selected from the group consisting of anionic, nonionic, cationic, amphoteric, zwitterionic surfactants, and mixtures thereof. Other adjunct materials may be present. These compounds can also be presented in a liquid base, for a hard surface, or other surface bleaching execution. These compounds may be useful for pulp and textile bleaching processing. Each of these compounds, and adjunct materials suitable for use herein are further discussed below:

#### a. Builders

The builders are typically alkaline builders, i.e., those which in aqueous solution will attain a pH of 7-14, preferably 9-12. Examples of inorganic builders include the alkali metal and ammonium carbonates (including sesquicarbonates and bicarbonates), phosphates (including orthophosphates, tripolyphosphates and tetrapyrophosphates), aluminosilicates (both natural and synthetic zeolites), and mixtures thereof. Carbonates are especially desirable for use in this invention because of their high alkalinity and effectiveness in removing hardness ions which may be present in hard water, as well as their low cost. Carbonates can be used as the

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predominate builder. Silicates ( $\text{Na}_2\text{O}:\text{SiO}_2$ , modulus of 4:1 to 1:1, most preferably about 3:1 to 1:1) can also be used. Silicates, because of their solubility in water and ability to form a glassy matrix, can also be advantageously used as a binder.

Organic builders are also suitable for use, and are selected from the group consisting of the alkali metal and ammonium sulfosuccinates, polyacrylates, polymaleates, copolymers of acrylic acid and maleic acid or maleic acid or maleic anhydride, citrates and mixtures thereof.

b. Fillers/Diluents

Fillers for the bleach composition are used to insure the correct amount or dose of cleaning activities is delivered per usage. Salts such as  $\text{NaCl}$ ,  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$ , and borax, are preferred. Organic diluents, such as sugar, are possible. If in a liquid execution, solvents (such as, without limitation, alkanols, glycols, glycol ethers, hydrocarbons, ketones, and carboxylic acids), liquid surfactants and water could be used as diluents.

c. Surfactants

Surfactants will generally be added to bleach for removal of particular targeted soils, e.g., nonionic surfactants on oily substrates, and anionic surfactants on particulate substrates. However, generally speaking, oxidant bleach compositions may contain little or even no surfactant.

Particularly effective surfactants appear to be anionic surfactants. Examples of such anionic surfactants may include the ammonium, substituted ammonium (e.g., mono-, di-, and tri-ethanolammonium), alkali metal and alkaline earth metal salts of  $\text{C}_6$ - $\text{C}_{20}$  fatty acids and rosin acids, linear and branched alkyl

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benzene sulfonates, alkyl sulfates, alkyl ether sulfates, alkane sulfonates, olefin sulfonates, hydroxyalkane sulfonates, fatty acid monoglyceride sulfates, alkyl glyceryl ether sulfates, acyl  
5 sarcosinates and acyl N-methyltaurides. Preferred are alkylaryl sulfonated surfactants, such as alkylbenzene sulfonates.

Other preferred surfactants of use include linear ethoxylated alcohols, such as those sold by  
10 Shell Chemical Company under the brand name NEODOL. Other suitable nonionic surfactants can include other linear ethoxylated alcohols with an average length of 6 to 16 carbon atoms and averaging about 2 to 20 moles of ethylene oxide per mole of alcohol; linear and  
15 branched, primary and secondary ethoxylated, propoxylated alcohols with an average length of about 6 to 16 carbon atoms and averaging 0-10 moles of ethylene oxide and about 1 to 10 moles of propylene oxide per mole of alcohol; linear and branched alkylphenoxy  
20 (polyethoxy) alcohols, otherwise known as ethoxylated alkylphenols, with an average chain length of 8 to 16 carbon atoms and averaging 1.5 to 30 moles of ethylene oxide per mole of alcohol; and mixtures thereof.

Further suitable nonionic surfactants may  
25 include polyoxyethylene carboxylic acid esters, fatty acid glycerol esters, fatty acid and ethoxylated fatty acid alkanolamides, certain block copolymers of propylene oxide and ethylene oxide, and block polymers of propylene oxide and ethylene oxide with propoxylated  
30 ethylene diamine. Also included are such semi-polar nonionic surfactants like amine oxides, phosphine oxides, sulfoxides, and their ethoxylated derivatives.

Suitable cationic surfactants may include the quaternary ammonium compounds in which typically one of

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the groups linked to the nitrogen atom is a C<sub>12</sub>-C<sub>18</sub> alkyl group and the other three groups are short chained alkyl groups which may bear substituents such as phenyl groups.

5 Further, suitable amphoteric and zwitterionic surfactants which contain an anionic water-solubilizing group, a cationic group and a hydrophobic organic group may include amino carboxylic acids and their salts, amino dicarboxylic acids and their salts,  
10 alkylbetaines, alkyl aminopropylbetaines, sulfobetaines, alkyl imidazolinium derivatives, certain quaternary ammonium compounds, certain quaternary phosphonium compounds and certain tertiary sulfonium compounds.

15 Further examples of anionic, nonionic, cationic and amphoteric surfactants which may be suitable for use in this invention are depicted in Kirk-Othmer, Encyclopedia of Chemical Technology, Third Edition, Volume 22, pages 347-387, and McCutcheon's  
20 Detergents and Emulsifiers, North American Edition, 1983, which are incorporated herein by reference.

#### d. Chelating Agents

In some of the compositions herein, it is especially preferred to include a chelating agent, most  
25 preferably, an aminopolyphosphonate. These chelating agents assist in maintaining the solution stability of the oxidant in order to achieve optimum performance. In this manner, they are acting to chelate free heavy metal ions. The chelating agent is selected from a  
30 number of known agents which are effective at chelating free heavy metal ions. The chelating agent should be resistant to hydrolysis and rapid oxidation by oxidants. Preferably, it should have an acid dissociation constant (pK<sub>a</sub>) of 1-9, indicating that it



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dissociates at low pH's to enhance binding to metal cations. The most preferred chelating agent is an aminopolyphosphonate which is commercially available under the trademark DEQUEST, from Monsanto Company.

5 Examples thereof are DEQUEST 2000, 2041, 2060 and 2066. A polyphosphonate, such as DEQUEST 2010, is also suitable for use. Other chelating agents, such as ethylenediaminetetraacetic acid (EDTA) and  
10 nitrilotriacetic acid (NTA) may also be suitable for use. Still other new, preferred chelating agents are new propylenediaminetetraacetates, such as Hampshire 1,3 PDTA, from W.R. Grace, and Chel DTPA 100#F, from Ciba-Geigy A.G. Mixtures of the foregoing may be suitable. Effective amounts of the chelating agent  
15 range from 1-1,000, more preferably 5-500, most preferably 10-100 ppm chelating agent in the wash liquor.

e. Other Adjuncts:

20 The standard oxidant bleach adjuncts can be included in the present invention.

These include enzymes are especially desirable adjunct materials in oxidant bleach products. However, it may be preferred to include an enzyme stabilizer.

25 Proteases are one especially preferred class of enzymes. They are selected from acidic, neutral and alkaline proteases. The terms "acidic," "neutral," and "alkaline," refer to the pH at which the enzymes' activity are optimal. Examples of neutral proteases  
30 include MILEZYME (available from Miles Laboratory) and trypsin, a naturally occurring protease. Alkaline proteases are available from a wide variety of sources, and are typically produced from various microorganisms (e.g., Bacillus subtilis). Typical examples of

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alkaline proteases include MAXATASE and MAXACAL from International BioSynthetics, ALCALASE, SAVINASE and ESPERASE, all available from Novo Industri A/S. See also Stanislawski et al., U.S. Patent No. 4,511,490, incorporated herein by reference.

Further suitable enzymes are amylases, which are carbohydrate- hydrolyzing enzymes. It is also preferred to include mixtures of amylases and proteases. Suitable amylases include RAPIDASE, from Societe Rapidase, MILEZYME from Miles Laboratory, and MAXAMYL from International BioSynthetics.

Yet other suitable enzymes are lipases, such as those described in Silver, U.S. Patent No. 3,950,277, and Thom et al., U.S. Patent No. 4,707,291, both incorporated herein by reference.

Still further enzymes of interest herein are peroxidases, such as horseradish peroxidase, and those disclosed in International Patent Publication WO 93/24628, incorporated herein by reference. Mixtures of any of the foregoing hydrolases are desirable, especially protease/amylase blends.

Additionally, optional adjuncts include dyes, such as Monastral blue and anthraquinone dyes (such as those described in Zielske, U.S. Patent No. 4,661,293, and U.S. Patent No. 4,746,461).

Pigments, which are also suitable colorants, can be selected, without limitation, from titanium dioxide, ultramarine blue (see also, Chang et al., U.S. Patent No. 4,708,816), and colored aluminosilicates.

Fluorescent whitening agents are still other desirable adjuncts. These include the stilbene, styrene, and naphthalene derivatives, which upon being impinged by ultraviolet light, emit or fluoresce light in the visible wavelength.

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Additional organic bleach activators can be added, including, but not limited to, esters (see Fong et al., U.S. Patent No. 4,778,618 and Rowland et al., U.S. Patent No. 5,182,045), ketones, imides (See Kaaret, U.S. Patent No. 5,478,569) and nitriles, each of which are incorporated herein by reference.

The additives may be present in amounts ranging from 0-50%, more preferably 0-30%, and most preferably 0-10%. In certain cases, some of the individual adjuncts may overlap in other categories. However, the present invention contemplates each of the adjuncts as providing discrete performance benefits in their various categories.

#### EXPERIMENTAL SECTION

##### Syntheses of Oxidatively Robust Tetraamido Ligands.

**Materials.** All solvents and reagents were reagent grade (Aldrich, Aldrich Sure-Seal, Fisher) and were used as received. Microanalyses were performed by Midwest Microlabs, Indianapolis, IN.

**Mass Spectrometry.** Electrospray ionization mass spectra were acquired on a FINNIGAN-MAT SSQ700 (San Jose, CA) mass spectrometer fitted with an ANALYTICA OF BRANFORD electrospray interface. Electrospray voltages of 2400-3400 V were utilized. Samples were dissolved in either acetonitrile or dichloromethane at concentrations of approximately 10 pmol/ $\mu$ l and were introduced into the ESI interface prior to data acquisition by direct infusion at a flow rate of 1 l/min and were introduced prior to data acquisition. Positive ion electron impact ionization (70 ev) MS experiments were performed on a FINNIGAN-MAT 4615 quadrupole mass spectrometer in conjunction with an INCOS data system. The ion source temperature was 150°C and the manifold chamber temperature was 100°C.

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Sample introduction was by means of a gas chromatograph or a direct insertion probe. Positive ion fast atom bombardment mass spectra were acquired on a FINNIGAN-MAT 212 magnetic sector instrument in combination with an INCOS data system. The accelerating voltage was 3 kV and the ion source temperature was approximately 70°C. An ION TECH saddle field fast atom gun was employed with xenon at 8 keV. Thioglycerol was utilized as the FAB matrix. Positive ion electron impact ionization (70 eV) MS/MS experiments were performed on a FINNIGAN-MAT TSQ/700 tandem quadrupole mass spectrometer. Sample introduction was by means of a direct insertion probe. The ion source was maintained at 150°C. and the manifold chamber was held at 70°C. Collision-induced dissociation (CID) was achieved by introducing argon into the center rf-only collision octapole until the pressure in the manifold reached  $0.9-2.5 \times 10^{-6}$  Torr. The nominal ion kinetic energy for CID product ions was <35 eV (laboratory reference). High resolution data were obtained on a JEOL JMS AX-505H double focusing mass spectrometer in the EB configuration using a resolution of 7500. Sample introduction was by means of a gas chromatograph or direct insertion probe. During mass spectral acquisition, perfluorokerosene was introduced into the ion source by means of a heated inlet. Exact mass assignments were obtained by computer-assisted interpolation from the masses of perfluorokerosene. GC/MS conditions: column, 20 m x 0.25 mm DB-1701 (J & W Scientific); carrier gas, helium with a linear velocity of 40 cm/sec; injector, 125°C; column temperature, 35°C for 3 min, followed by an increase at 10°C/min to 100°C; injection, split mode, appx. 50:1 ratio.

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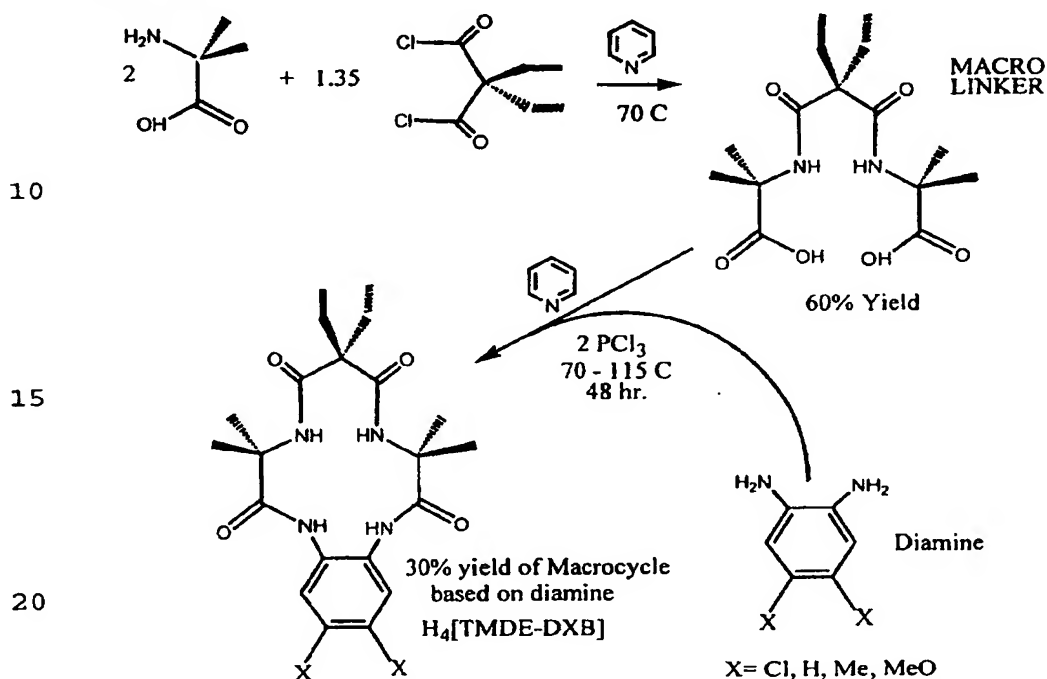
**Spectroscopic Methods.** 300 MHz  $^1\text{H}$  NMR spectra and 75 MHz  $^{13}\text{C}$  NMR spectra were obtained on an IBM AF300 instrument using an OXFORD Superconducting magnet system, data acquisition was controlled by  
5 BRUKER software. Infrared spectra were obtained on a MATTSON GALAXY Series 5000 FTIR spectrometer controlled by a MACINTOSH II computer. UV/vis spectra were obtained on a HEWLETT PACKARD 8452A spectrophotometer driven by a ZENITH Z-425/SX computer. Conventional X-  
10 Band EPR spectra were recorded on a BRUKER ER300 spectrometer equipped with an OXFORD ESR-900 helium flow cryostat. Mossbauer spectra were obtained on constant acceleration instruments and isomeric shifts are reported relative to an iron metal standard at 298  
15 K. In order to avoid orientation of polycrystalline samples by the applied magnetic field, the samples were suspended in frozen nujol.

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# Syntheses of Macrocyclic Tetraamido-N Donors Ligands

## General Reaction Scheme

Depicted below is the preferred reaction sequence for synthesizing the inventive macrocyclic tetraamido ligands:



An  $\alpha$ -amino carboxylic acid is mixed with an activated malonate in pyridine at temperatures less than  $70^\circ\text{C}$ . After the selective double coupling reaction is complete, 72-144 hrs., the MACRO LINKER (A-L-A) is isolated. In a second step, a diamine, preferably an o-phenylene diamine, is added to a pyridine solution of the MACRO LINKER in the presence of a coupling agent, preferably  $\text{PCl}_3$ , or pivaloyl chloride. The ring closure (a double coupling) reaction is allowed to proceed at reflux for 48-110 hrs., and then the desired macrocyclic tetraamide is isolated in good yield.

**SUBSTITUTE SHEET (RULE 26)**

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In the following Examples 1-25, various portions of the reaction steps are portrayed. Examples 26-39 demonstrate performance attributes and advantages of the invention for oxidation reactions involving lignin bleaching and dye bleaching.

#### Example 1

Macro Linker Intermediate (A-L-A) synthesis, from  $\alpha$ -methyl alanine and diethyl malonyl dichloride (a Tetramethyl Diethyl substituted intermediate).

A two-neck flask (1 L) fitted with a pressure equalizing addition funnel (250 mL) and a septum is placed under  $N_2$   $\alpha$ -amino isobutyric acid (i.e.  $\alpha$ -methyl alanine) (20.62 g, 0.2 mol) and dry pyridine (250 mL, dried over 4 Å mol sieves) are added to the flask and heated 60-70°C with stirring, then diethyl malonyl dichloride (23.23 mL, 0.135 mol) dissolved in dry pyridine (100 mL, dried over 4 Å mol sieves) is added to the addition funnel. The contents of the addition funnel are added (dropwise, 1 h) to the reaction and the acylation allowed to proceed (60-70°C, 30-36 h) under  $N_2$  or with a drying tube fitted. Once the acylation is complete the reaction is quenched by adding  $H_2O$  (30 mL) and stirring (60-70°C, 24 h). The solvent volume is reduced on the rotary evaporator to give an oil, then HCl (conc., ca. 25 mL) is added to a final pH of 2-3. The hot solution is set in the refrigerator (4°C, 15 h), and the resulting tan product collected by frit filtration, and washed thoroughly with acetonitrile (2 x 100 mL). The air-dried white product (16.5 - 19.8 g, 50-60% yield) should be stored in a dessicator. This product is usually pure enough for ring closure reactions, but recrystallization may occasionally be required. Characterization:  $^1H$  NMR

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spectrum ( $d^2$ -pyridine)  $\delta$  [ppm]: 8.9 (s, 2H, NH amide); 2.2 (q, 4H); 1.8 (s, 12H); 1.2 (t, 6H). IR(Nujol mull):  $\nu$  [ $cm^{-1}$ ] = 3310 (amide NH); 1721 (carboxylic CO); 1623 (amide CO). Anal. Calcd for  $C_{15}H_{21}N_2O_6$ ; C, 54.53; H, 7.93; N, 8.48. Found: C, 54.48; H, 7.88; N, 8.47.

#### Example 2

Large Scale, Macro Linker Intermediate (A-L-A) synthesis, from  $\alpha$ -methyl alanine and diethyl malonyl dichloride (a TMDE substituted intermediate).

10                   A two-neck flask (2 L, RB + Claisen) fitted with a pressure equalizing addition funnel (250 mL) and septa, is placed under  $N_2$ .  $\alpha$ -aminoisobutyric acid (i.e.  $\alpha$ -methyl alanine) (90.3 g, 0.9 mol) is added, anhydrous pyridine (1.4 L, sure seal) is cannulated into the  
15 flask and the reaction mix heated to 45-55°C and stirred. Pyridine (100 mL, sure seal) and then diethyl malonyl dichloride (104.4 mL, 0.61 mol) are cannulated into the addition funnel. The contents of the addition funnel are added (dropwise, 3-4 h) to the reaction, the  
20 addition funnel is then removed, and the acylation allowed to proceed (55-65°C, 120-130 h) under  $N_2$ . Once the acylation is complete the reaction is quenched by adding  $H_2O$  (100 mL) and stirring (60-70°C, 24-36 h). The solvent volume is reduced on the rotary evaporator  
25 to give an oil, then HCl (conc., ca. 110 mL) is added to a final pH of 2-3. The hot solution is set in the refrigerator (4°C, 15 h), and the resulting tan product collected by frit filtration, and washed thoroughly with acetonitrile (700 mL, 150 mL) by stirring in an  
30 erlenmeyer flask. The air-dried white product (87.9 g, 60% yield), is crushed in a mortar and pestle and stored in a dessicator. The large scale reaction amide intermediate product is more likely to need recrystallization before use in ring closure reactions.



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Example 3

Recrystallization of the TMDE substituted intermediate  
Crude TMDE intermediate from Example 2 (50.4 g., 0.153  
mol) is dissolved in H<sub>2</sub>O (500 mL, deionized) by adding  
5 Na<sub>2</sub>CO<sub>3</sub> (16.2 g, 0.153 mol) in three aliquots slowly and  
carefully to avoid excessive frothing, with good  
stirring and mild heating. The solution is brought to  
a boil, filtered and acidified with HCl (conc., 30 mL,  
0.36 mol). The solution is allowed to cool (overnight,  
10 4°C) and the white precipitate filtered off and washing  
with acetonitrile (250 mL). The air dried product  
(38.8-45.4 g, recryst. yield 77-90%) should be stored  
in a dessicator.

Example 4

15 Hexa Methyl (HM) Intermediate (A-L-A)

The synthesis of the HM intermediate is  
identical to that for the TMDE intermediate in Example  
2 with the following exceptions, dimethyl malonyl  
dichloride (17.8 mL, 0.135 mol) is substituted for  
20 diethyl malonyl dichloride, and the reaction  
temperature must be decreased to 55-65°C due to the  
lower boiling point of the acylating agent. The yield  
of hexamethyl intermediate is 45-60%.  
Characterization: <sup>1</sup>H NMR (d<sup>5</sup> pyridine, δ [ppm]); 9/2-9.8  
25 br s, 2 H (carboxylic OH), 8.23 s, 2 H (amide), 1.87 s  
12 H (CH<sub>3</sub>), 1.74 s 6 H (CH<sub>3</sub>). IR (nujol/NaCl) ν[cm<sup>-1</sup>];  
3317.0 (amide NH); 1717.9 (carboxylic CO); 1625.7  
(amide CO). Anal. (dried at 100°C) Calcd. for C<sub>13</sub>H<sub>22</sub>N<sub>2</sub>O<sub>6</sub>;  
C 51.63, H 7.34, N 9.27. Found; C 51.64, H 7.35, N  
30 9.33.

Example 5

Recrystallization of HM Intermediate  
Crude hexamethyl (HM) intermediate was  
recrystallized in the same manner as the TMDE amide

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intermediate. Due to the slightly higher water solubility of the HM amide intermediate a little less H<sub>2</sub>O should be employed.

Example 6

5 Di CyHex Di Ethyl Intermediate

A round bottom flask (500 mL), is charged with 1-amino-1-cyclohexane carboxylic acid (15 g, 0.1 mol), then fitted with a pressure equalizing addition funnel (40 mL), capped with a septum, and purged with  
10 nitrogen. Anhydrous pyridine (300 mL) is cannulated into the reaction flask through the addition funnel, and 20 mL into the addition funnel. Start heating the system and stabilize the temperature at 60°C. Once 60°C is reached, one-third of the total diethyl malonyl  
15 dichloride to be utilized in the reaction (i.e. 6 mL, 0.033 mol) is added via syringe to the addition flask. The mixture of pyridine/diethyl malonyl dichloride is added dropwise to the reaction and the acylation allowed to proceed for 12 hours. A second (6 mL, 0.033  
20 mol) and third aliquot (6 mL, 0.033 mol) are added at 12 hour intervals. After all of the acylating agent has been added and allowed to react (total reaction time 48-56 h), 20 mL of water is added dropwise to the reaction. The reaction is heated for an additional 24  
25 hours to ring open the mono and bis oxazalone intermediates and yield the diamide dicarboxylic acid. Removal of the pyridine by rotary evaporation yields a pale yellowish tan sludge which is acidified to pH 2 with HCl(conc.). The crude product is collected by  
30 filtration, washed with acetonitrile and air dried to yield the white DiCyHexDE-amide intermediate (16 g, 74%). Characterization: <sup>1</sup>H NMR (d<sup>5</sup>-pyridine) δ [ppm]: 8.30 (s, 2H, NH amide), 2.60 (m, 4 H, cyhex), 2.25 (q, 4 H, ethyl CH<sub>2</sub>), 2.15 (m, 4 H, cyhex), 1.8-1.5 (m, 10 H,

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cyhex), 1.25 (m, 2 H, cyhex), 1.20 (t, 6 H, ethyl CH<sub>3</sub>).  
13C NMR broadband decoupled (d<sup>5</sup>-pyridine) δ [ppm]:  
178.0, (carboxylic CO), 174.3 (amide CO), 60.5 (cyhex  
quat), 59.4 (malonyl quat), 33.0 (cyhex α CH<sub>2</sub>), 30.3  
5 (ethyl CH<sub>2</sub>) 26.0 (cyhex γ CH<sub>2</sub>), 22.3 (cyhex β CH<sub>2</sub>), 9.9  
(ethyl CH<sub>3</sub>). IR (nujol/NaCl) ν [cm<sup>-1</sup>]: 3307 (amide NH);  
3150 (sh, br, m, amide NH/carboxylic OH), 3057 (s, str,  
H bonded amide NH/carboxylic OH), 1717 (s, str,  
carboxylic CO); 1621 (s, str, amide CO). Anal. Calcd  
10 for C<sub>21</sub>H<sub>34</sub>N<sub>2</sub>O<sub>6</sub>: C, 61.44; H, 8.35; N, 6.82. Found: C,  
61.41; H, 8.38, N, 6.90%.

#### Example 7

##### Di CyHex Diethyl Mono Oxazalone

##### Failure to quench the Di CyHex Di Ethyl

15 Intermediate Reaction (with heat & water, see above) at  
a stoichiometry of 1.35 diethyl malonyl dichloride; 2  
CY Hex amino acid, leads to a mixture of the DiCyHexDE-  
amide intermediate and mono oxazalone products. The  
DiCyHexDE Mono Oxazalone product is moderately soluble  
20 in boiling cyclohexane while the cyclohexyl amide  
intermediate is not, allowing for a simple separation  
of the product mixture, ca. 10 g of mixed amide  
intermediate and mono oxazalone containing some  
residual CH<sub>2</sub>Cl<sub>2</sub> was boiled with vigorous stirring in  
25 400-500 mL cyclohexane. The insoluble DiCyHexDE-amide  
intermediate product was collected by hot gravity  
filtration while the mono oxazalone product  
crystallized out gradually as the cyclohexane solution  
cooled and evaporated. Yield amide intermediate ca. 6  
30 g, yield mono oxazalone ca. 4 g. Characterization of  
the mono oxazalone: <sup>1</sup>H NMR (d<sup>5</sup>-pyridine) δ [ppm]: 9.7  
(s, 1H, amide NH), 2.7-1.6 (unresolved Cy Hex groups),  
1.05 (t, 6 H, ethyl CH<sub>3</sub>). IR (nujol/NaCl) [cm<sup>-1</sup>]: 3309  
(sh, w, amide NH), 3229 (s, str, H bonded amide

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NH/carboxylic OH), 3166 (s, str, H bonded amide  
NH/carboxylic OH), 3083 (s, str, H bonded amide  
NH/carboxylic OH), 1834 (s, str, oxaz C=O), 1809 (s, m,  
H bonded oxaz C=O), 1743 (s, str, carboxylic CO), 1663  
5 (s, str, oxaz C=N), 1639 (s, br, str, amide CO). Anal.  
Calcd for  $C_{21}H_{32}N_2O_5 \cdot (C_6H_{12})_{0.25}$ : C, 65.35; H, 8.53; N,  
6.77. Found: C, 65.07; H 8.67; N, 6.68%. Presence of  
solvate cyclohexane was confirmed by  $^{13}C$  NMR.

10

#### Macrocyclization Reactions

Examples of several synthetic routes for the  
preparation of macrocyclic tetraamido ligands follow.

##### **Phosphorus Trichloride Coupling**

15 Phosphorus trichloride coupling of the amide-  
containing intermediate (A-L-A) to aromatic 1,2-  
diamines yields macrocyclic tetraamides safely, cheaply  
and in high yield. Two distinct variations of the PCl,  
coupling method are useful, the differences relate to  
the order of addition and choice of reagents utilized.  
20 These methods are applicable to the preparation of a  
wide variety of different macrocycles with different  
electronic substituents present on the bridge diamine,  
or steric substituents present on the amide  
intermediate, primarily because of the parallel  
25 incorporation of the macro linker type of amide  
intermediates into all of the syntheses.

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Example 8A. Macrocycle Synthesis via  $\text{PCl}_3$  Coupling

A long neck flask (250 mL) is charged with the amide intermediate of Examples 2-7, (10 mmol) a stir bar and then baked in the oven (80-100°C, 30-45 mins). The hot flask is placed under  $\text{N}_2$ , aryl diamine (10 mmol) is added and anhydrous pyridine (50 mL, sure seal) cannulated in. The flask is heated (50-60°C) and  $\text{PCl}_3$  (d = 1.574 g/mL, 1.72 mL, 20 mmol) syringed in as quickly as possible without excessive refluxing. This is an exothermic reaction; so caution should be used. The temperature is then increased to reflux or just below reflux (100-115°C) and the reaction allowed to proceed under  $\text{N}_2$  (48 h). After the acylation is complete, the contents of the flask are acidified with HCl (1 eq., ca. 60 mL) to a final pH 2. The mixture is transferred to an erlenmeyer (water is used to rinse the flask) and stirred with  $\text{CH}_2\text{Cl}_2$  (300 mL, 2-3h), then extracted with additional  $\text{CH}_2\text{Cl}_2$  (2 x 150 mL). The combined organic layers are washed with dilute HCl (0.1 M, 2 x 100 mL) followed by dilute aqueous  $\text{Na}_2\text{CO}_3$  (2 x 5g/100 mL). The organic solvents are removed on the rotary evaporator to yield crude product (30%). The weight of crude product is usually equivalent to the initial weight of diamine.

B. Macrocycle Synthesis via  $\text{PCl}_3$ , Coupling

A long neck flask (250 mL) is charged with  $\text{MgSO}_4$  (5 g), a stir bar, aryl diamine (10 mmol) and pyridine (50 mL, dried over 4 Å mol sieves) then placed under  $\text{N}_2$ .  $\text{PCl}_3$  (d = 1.754 g/mL, 1.72 mL, 20 mmol) is added via syringe and the mixture brought to reflux for 30 mins, an orange/yellow precipitate forms. The mixture is cooled somewhat, an amide intermediate (10 mmol) is added, then the mixture is refluxed under  $\text{N}_2$ .

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(115°C, 48 h). After the acylation is complete, the contents of the flask are acidified with HCl (1 eq., ca. 60 mL) to a final pH 2. The mixture is transferred to an erlenmeyer and stirred with CH<sub>2</sub>Cl<sub>2</sub> (2 x 150 mL).

5 The combined organic layers are washed with dilute HCl (0.1 M, 2 x 100 mL) followed by dilute Na<sub>2</sub>CO<sub>3</sub> (2 x 5g/100mL). The organic solvents are removed on the rotary evaporator to yield crude product (30%). The weight of crude product is usually equivalent to the  
10 initial weight of diamine.

Note: For larger scale macrocyclization reactions, the ring closure times are increased to 4-5 days at reflux, and most of the pyridine present at the end of the reaction is removed via rotary evaporation  
15 prior to acidification.

#### Example 9

TMDE-DCB from TMDE Intermediate + DCB Diamine

1,2-Diamino-4,5 dichlorobenzene (1.77 g, 10 mmol) was utilized as the aryl diamine with TMDE amide  
20 intermediate (3.3 g, 10 mmol) in the PCl<sub>3</sub> method A or B macrocyclization reaction. The crude macrocyclic product (2.7 g) was recrystallized from a minimum amount of hot 95% EtOH by evaporation to yield pure TMDE-DCB (1.5 g, 32%). Characterization: <sup>1</sup>H NMR  
25 (CD<sub>2</sub>Cl<sub>2</sub>) δ [ppm]: 7.65 (s, 1 H, ArH), 7.35 (s, 2 H, amide NH), 6.45 (s, 2H, amide NH), 1.90 (q, 4 H, ethyl CH<sub>2</sub>), 1.57 (s, 12 H, RCH<sub>3</sub>), 0.85 (t, 6H, ethyl CH<sub>3</sub>). IR (nujol/NaCl) ν[cm<sup>-1</sup>]: 3454 (trace ROH), 3346 (br, amide NH), 1706&1688&1645 (amide CO). Anal. Calcd. for  
30 C<sub>21</sub>H<sub>28</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>4</sub>; C, 53.51; H, 5.99; N, 11.89. Found C, 53.58; H, 6.09; N, 11.89.

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Example 10

TMDE-B from TMDE Intermediate + B Diamine

1,2-Diaminobenzene (i.e, o-phenylene  
diamine) (1.08 g, 10 mmol) was utilized as the aryl  
5 diamine with the TMDE amide intermediate (3.3 g, 10  
mmol) in the PCl<sub>3</sub> method A or B macrocyclization  
reaction. The crude macrocyclic product (1.5 g) was  
recrystallized from a minimum amount of hot 95% EtOH by  
evaporation to yield pure TMDE-B (25% from diamine).  
10 Characterization: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ [ppm]; 7.55 (m, 2 H,  
ArH), 7.48 (s, br, 2 H, aryl amide NH), 7.17 (m, 2 H,  
ArH), 6.46 (s, br, 2 H, alkyl amide NH), 2.07 (m, br, 4  
H, ethyl CH<sub>2</sub>), 1.60 (s, 12 H, RCH<sub>3</sub>), 0.89 (t, 6 H, ethyl  
CH<sub>3</sub>). IR (nujol/NaCl) [cm<sup>-1</sup>]; 3395&3363 (amide NH),  
15 1702&1680&1652&1635 (amide CO). Anal. Calcd. for  
CH<sub>21</sub>H<sub>10</sub>N<sub>4</sub>O<sub>4</sub>.H<sub>2</sub>O: C, 59.98; H, 7.67; N, 13.32. Found: C,  
60.18; H, 7.20; N, 13.18.

Example 11

TMDE-DMB from TMDE Intermediate + DMB Diamine

1,2-Diamino-4,5-Dimethylbenzene (1.36 g, 10  
20 mmol) was utilized as the aryl diamine with Tetramethyl  
Diethyl amide intermediate (3.3 g, 10 mmol) in the PCl<sub>3</sub>  
method A or B macrocyclization reaction. The crude  
macrocyclic product (1.6 g) was recrystallized from a  
25 minimum amount of hot 95% EtOH by evaporation to yield  
pure TMDE-DMB (25% from diamine). Characterization: <sup>1</sup>H  
NMR (DMSO d<sub>6</sub>) δ [ppm]: 8.00 (s, 2 H, amide NH), 7.67 (s,  
2 H, amide NH), 7.28 (s, 2 H, ArH), 2.17 (s, 6 H, aryl  
CH<sub>3</sub>), 1.99 (q, 4 H, ethyl CH<sub>2</sub>), 1.46 (s, 12 H, RCH<sub>3</sub>),  
30 0.75 (t, 6 H, ethyl CH<sub>3</sub>). IR (nujol/NaCl) ν [cm<sup>-1</sup>]:  
3446 (s, m, trace ROH), 3362 (s, str, amide NH), 3348  
(sh, m, amide NH), 3332 (s, str, H amide NH), 1696  
(amide CO), 1679 (amide CO), 1651 (amide CO), 1641  
(amide CO), 1584 (s, m/w, aryl ring/amide). Anal.

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Calcd. for  $C_{23}H_{34}N_4O_4$ : C, 64.16; H, 7.96; N, 13.01, Found: C, 64.09, 64.28; H, 8.04, 7.92; N, 12.86, 13.04.

#### Example 12

TMDE-DMOB from TMDE Amide Intermediate + DMOB Diamine  
5                   1,2-Diamino-4,5-Dimethoxybenzene. 2 HBr (5.0 g, 15 mmol) prepared as above was utilized as the aryl diamine directly with the Tetramethyl Diethyl amide intermediate (5.0 g, 15 mmol) in a 1.5 scale PCl, method A or B macrocyclization reaction. The crude  
10 macrocyclic product (3.57 g) was recrystallized from a minimum amount of hot 80-85% EtOH (1 g/40 mL) by evaporation to yield pure TMDE-DMOB (30% from diamine). Characterization:  $^1H$  NMR ( $CD_2Cl_2$ ) [ppm]: 7.26 (s, 2 H, amide NH), 7.01 (s, 2 H, ArH), 6.41 (s, 2 H, amide NH),  
15 3.80 (s, 6H, aryl  $OCH_3$ ), 2.07 (q, br, 4 H, ethyl  $CH_2$ ), 1.54 (s, 12 H,  $RCH_3$ ), 0.90 (t, 6 H, ethyl  $CH_3$ ). IR (nujo/NaCl)  $\nu$  [ $cm^{-1}$ ]: 3451 (s, m, H bonded  $H_2O$ ), 3391&3347 (amide NH), 1695&1670&1655 (amide CO). Anal. Calcd. for  $C_{23}H_{34}N_4O_6 \cdot (H_2O)_{0.33}$ : C, 58.96; H, 7.46; N,  
20 11.96, Found (ESU); C, 58.90; H, 7.26; N, 11.76. Presence of solvate  $H_2O$  was confirmed by  $^1H$  NMR and IR.

#### Example 13

TMDE-Nap from TMDE Intermediate + Nap Diamine  
25                   4,5 Diamino Napthalene (1.68 g, 10 mmol) was utilized as the aryl diamine with the Tetramethyl Diethyl amide intermediate (3.3 g, 10 mmol) in the PCl, method A or B macrocyclization reaction. Unoptimized yield was 15-20% from diamine.  $^1H$  NMR ( $CDCl_3$ )  $\delta$  [ppm]:  
30 8.05 (s, 2 H, ArH  $\alpha$  ring), 7.75 (m, 2H, ArH  $\beta$  ring), 7.55 (s, 2 H, Ar amide NH), 7.35 (m, 2H, ArH  $\beta$  ring), 6.45 (s, 2 H, alkyl amide NH), 2.15 (m, br, 4 H, ethyl  $CH_2$ ), 1.65 (s, 12 H,  $RCH_3$ ), 0.90 (t, 6 H, ethyl  $CH_3$ ).



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Example 14

HM-DCB from HM Intermediate + DCB Diamine

1,2-Diamino-4,5-Dichlorobenzene (1.77 g, 10 mmol) was utilized as the diamine with Hexa Methyl amide intermediate (3.02 g, 10mmol) in the  $\text{PCl}_3$ , method A or B macrocyclization reaction. The crude macrocycle (1.33g, 30%) was recrystallized from a minimum of hot n-propanol by evaporation, 1st crop recrystallization yield was 60%. Characterization:  $^1\text{H}$  NMR  $\delta$  [ppm]: 7.69 (s, 2 H, ArH), 7.39 (s, 2 H, amide NH), 6.44 (s, 2 H, amide NH), 1.58 (s, 12 H, arm methyls), 1.53 (s, 6 H, malonate methyls), small n-propanol peaks were noted. IR (nujol/NaCl)  $\nu$  [ $\text{cm}^{-1}$ ]: 3503 (s, br, m-w, n-propanol OH), 3381 (sh, m, amide NH), 3338 (s, str, amide NH), 1689 (s, str, amide CO), 1643 (s, str, amide CO). Anal. Calcd. for  $\text{C}_{19}\text{H}_{24}\text{N}_4\text{O}_4\text{Cl}_2 \cdot (\text{C}_3\text{H}_8\text{O})_{0.2}$ : C, 51.70; H, 5.57, N, 12.30%. Found C, 51.69; H, 5.63; N, 12.33%.

Example 15

HM-DMOB and HM-B from HM Intermediate + DMOB or B Diamine

The HM intermediate has also been used to synthesize HM-B and HM-DMOB according to the same method and with similar results to those obtained in example 14 for the dichloro derivative.  $^1\text{H}$  NMR data for HM-DMOB in  $\text{CDCl}_3$ ,  $\delta$  [ppm]: 7.65 (s, 2H, amide NH), 7.21 (s, 2 H, aryl CH), 6.72 (s, 2 H, amide NH), 4.00 (s, 6 H, methoxy  $\text{CH}_3$ ), 1.76 (s, 12 H, arm methyls), 1.58 (s, 6 H, malonate methyls).  $^1\text{H}$  NMR data for HM-B in  $\text{d}^5$  pyridine  $\delta$  [ppm]: 8.55 (s, 2 H, amide NH), 8.40 (s, 2 H, amide NH), 7.81 (m, 2H, ArH aa'bb'), 7.10 (m, 2 H, ArH aa'bb'), 1.77 (s, 12 H, arm methyls), 1.73 (s, 6 H, malonate methyls). The amide peaks tend to shift a few tenths of a ppm in the presence of impurity species such as water, acids, etc.

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Example 16

DiCyHexDE-DCB from DiCyHexDE Intermediate + DCB Diamine  
1,2-Diamino-4,5-Dichlorobenzene (1.77 g, 10  
mmol) was utilized as the aryl diamine with Di Cy Hex  
5 Diethyl amide intermediate (3.3 g, 10 mmol) in the  $\text{PCl}_3$ ,  
method A or B macrocyclization reaction. Due to the  
increased steric hindrance an increased ring closure  
reaction time is recommended (3-4 days as opposed to  
the usual 48 h). Cy Hex Oxazolones formed as a side  
10 product during the reaction are not removed by the acid  
base workup, so it is necessary to triturate/wash the  
initially isolated  $\text{CH}_2\text{Cl}_2$  soluble product with pentane  
to remove the oxazolones. Evaporation of the pentane  
washes allows for recycling of the oxazolones. The  
15 crude pentane insoluble product was recrystallized by  
dissolving in  $\text{CH}_2\text{Cl}_2$  or  $\text{CHCl}_3$ , adding cyclohexane until  
slightly cloudy and then evaporating in air (1-2 days)  
to yield the white microcrystalline DiCyHexDE-DCB  
product, which was collected by filtration (1.38g, 25%  
20 from diamine). Recrystallization from hot neat toluene  
with evaporation also appears promising.  
Characterization:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  [ppm]: 7.70 (s, 2 H,  
ArH), 7.45 (s, 2 H, amide NH), 6.45 (s, 2 H, amide NH),  
2.35 (m, br, 4 H, cyhex), 2.00 (m, br,  $\approx$ 8 H,  
25 cyhex/ethyl  $\text{CH}_2$ ), 1.70 (m, br,  $\approx$  8 H, cyhex), 1.30 (m,  
br,  $\approx$  4 H, cyhex), 0.90 (t, 6 H, ethyl  $\text{CH}_3$ ). Anal.  
(Dried at  $100^\circ\text{C}$ ) Calcd. for  $\text{C}_{27}\text{H}_{36}\text{Cl}_2\text{N}_4\text{O}_4$ ,  $(\text{C}_6\text{H}_{12})_{0.2}$ : C,  
59.60; H, 6.81; N, 9.86, Found: C, 59.60; H, 6.77; N,  
9.77. Presence of solvent cyclohexane was confirmed by  
30  $^1\text{H}$  and  $^{13}\text{C}$  NMR.

Example 17

DiCyHexDE-B from DiCyHexDE Intermediate + B Diamine  
1,2-Diaminobenzene (ortho-phenylene diamine,  
1.08 g, 10 mmol) was utilized as the aryl diamine in a

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preparation analogous to that for DiCyHexDE-DCB, to yield DiCyHexDE-B (1.25 g, 26% from diamine). Characterization:  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  [ppm]: 7.62 (s, 2 H, aryl amide NH), 7.51 (m, 2 H, ArH), 7.18 (m, 2 H, ArH), 6.71 (s, 2 H, alkyl amide NH), 2.12 (m, 6H, Cyhex), 1.85 (q&m, ethyl  $\text{CH}_2$  & cyhex), 1.62 (m, cyhex), 1.37 (m, cyhex), 0.90 (t, 6 H, ethyl  $\text{CH}_3$ ), 0.85 (m, cyhex). IR (nujol/NaCl)  $\nu$  [ $\text{cm}^{-2}$ ]: 3750 (s, m,  $\text{H}_2\text{O}$ ), 3385 (s, str, amide NH), 314 (s, str, amide NH), 3258 (s, m, br, H bonded amide NH), 1694 (s, str, amide CO), 1651 (s, str, amide CO), 1594 (s, m, aryl ring/amide).

#### Example 18

##### DiCyHex Diethyl Bis Oxazalone

This product was obtained as a byproduct of the  $\text{PCl}_3$ , macrocyclization reaction of DiCyHex Di Ethyl Amide Intermediate with o-phenylene diamine. The bis oxazalone is not removed by the acid base workup (it is a neutral molecule and very organic soluble). Washing of the crude macrocyclic/oxazalone product with pentane extracts most of the bis oxazalone into the pentane. Air evaporation of the pentane layer yields the pure bis oxazalone as large (1 cm x 1 cm x 0.5 cm) transparent prisms. Due to the bulky hydrophobic CyHex groups this oxazalone is much more resistant to hydrolysis than the corresponding methyl derivative. Characterization of the bis oxazalone:  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  [ppm]: 2.05 (q, 4 H, ethyl  $\text{CH}_2$ ), 1.8-1.4 (Unresolved Cy Hex Groups), 0.88 (t, t H, ethyl  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR broadband decoupled ( $\text{CD}_3\text{CN}$ )  $\delta$  [ppm]: 181.0 (oxaz ( $\text{C}=\text{O}$ ), 162.7 (oxaz  $\text{C}=\text{N}$ ), 69.0 (oxaz cyhex quat), 49.0 (malonate quat), 34.3 (cyhex  $\alpha$  methylenes), 25.5 (cyhex  $\gamma$  methylenes), 24.9 (malonate methylenes), 21.8 (cyhex  $\beta$  methylenes), 8.3 (ethyl  $\text{CH}_3$ ). IR (nujol/NaCl)  $\nu$  [ $\text{cm}^{-1}$ ]: 1822 (s, str, br, oxaz  $\text{C}=\text{O}$ ), 1662 (s, str, oxaz

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C=N). Anal. (Dried at 50°C) Calcd. for  $C_{21}H_{30}N_2O_4$ : C, 67.36; H, 8.07; N, 7.48, Found: C, 67.26; H, 8.15; N, 7.64.

### Syntheses of Chelate Complexes

5

#### Example 19

$[Et_4N]2$  and  $[Et_4N]3$ , [the tetraethylammonium salts of iron(III) chloro TMDE-DCB monoanion and iron(III) aquo TMDE-DCB monoanion respectively].

10 The parent macrocyclic tetraamide of any of Examples 10-18 above (525 mg, 1.1mmol) is dissolved in tetrahydrofuran (40 mL, Aldrich) under  $N_2$ . Using schlenk techniques, tert-butyllithium (2.6 mL, 4.4 mmol, 1.7 M in 2,4-dimethylpentane, Aldrich) was added to the solution under  $N_2$  at -108°C. Ferrous chloride  
15 (anhydrous, 155 mg, 1.2 mmol, Alfa) was then added and the solution warmed to room temperature with stirring (16 h), to yield an olive-green precipitate, an air sensitive  $Fe^{II}$  complex. Air was admitted through a drying tube (2 h), and the orange solid was collected  
20 and washed with  $CH_2Cl_2$  (2 x 10 mL). The resulting orange powder was dried under reduced pressure. Yield: 595 mg (~93%). Because of variable solvation and limited solubility, the lithium salt was converted to the tetraethylammonium salt for further use. The  
25 lithium salt (595 mg) in  $CH_3OH$  (50 mL) was loaded on an ion exchange column (Dowex® 50X2-100, 25 g, 2 cm x 12.5 cm) that had been presaturated with  $[Et_4N]^+$  cations, and the orange band was eluted with  $CH_3OH$  (100 mL). The solvent was removed under reduced pressure. The  
30 residue was suspended in  $CH_2Cl_2$  (20 mL) and the mixture was filtered. The solvent was removed from the mother liquor under reduced pressure giving an orange hygroscopic glassy residue of  $[Et_4N]2$  that was used without further purification. IR (Nujol/NaCl,  $cm^{-1}$ ):

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1619 ( $\nu(\text{CO})$  amide), 1575 ( $\nu(\text{CO})$  amide), 1534  
( $\nu(\text{CO})$  amide). Careful purification of an iron(III)  
starting material was more conveniently approached by  
dealing with the axial aqua monoanionic complex rather  
5 than this axial chloro dianionic complex.  $[\text{Et}_4\text{N}]2$  (550  
mg, ca. 0.7 mmol) was dissolved in  $\text{CH}_3\text{CN}$  (50 mL).  
Silver tetrafluoroborate (140 mg, 0.7 mmol) was  
dissolved in  $\text{CH}_3\text{CN}$  (2 mL) and was added to the solution  
which was stirred (1 h). The  $\text{AgCl}$  precipitate was  
10 filtered off and the solvent removed under reduced  
pressure. The resulting  $[\text{Et}_4\text{N}]3$  was further purified by  
elution through a silica gel column (8%  $\text{MeOH}$  in  $\text{CH}_2\text{Cl}_2$ ).  
The solvent was removed under reduced pressure and the  
product was recrystallized from  $\text{H}_2\text{O}$ . Yield: 360 mg  
15 (~77% variable solvation with water was found in  
different microcrystalline samples). IR (Nujol/ $\text{NaCl}$ ,  $\text{cm}^{-1}$ ):  
1590 ( $\nu(\text{CO})$  amide), 1565 ( $\nu(\text{CO})$  amide), 1535 ( $\nu(\text{CO})$   
amide). Anal. Calcd for  $\text{C}_{29}\text{H}_{46}\text{N}_5\text{FeO}_5\text{Cl}_2 \cdot (\text{H}_2\text{O})$ : C, 50.52;  
H, 7.02; N, 10.16.; Cl, 10.28. Found: C, 50.24; H,  
20 6.84; N, 9.82; Cl, 10.32. ESIMS (negative ion):  $m/z$   
522.2,  $[3 - \text{H}_2\text{O}]^{1-}$  (100%);  $m/z$  269.7,  $[3 - \text{H}']^{2-}$  (18%).

#### Example 20

$[\text{Et}_4\text{N}]4$ , [the tetraethylammonium salt of iron(IV) chloro  
TMDE-DCB monoanion]  
25  $[\text{Et}_4\text{N}]2$  (500 mg, ca. 0.6 mmol) was dissolved  
in  $\text{CH}_2\text{Cl}_2$  (30 mL). Ammonium cerium(IV) nitrate (10.3 g,  
18.3 mmol) was added to the solution and the mixture  
was stirred (2 h). The solid cerium salts were removed  
by filtration. The purple product was obtained by  
30 removing the solvent under reduced pressure and drying  
under vacuum. Yield: 400 mg (~95%). Purple crystals  
were obtained by recrystallization from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ . IR  
(Nujol/ $\text{NaCl}$ ,  $\text{cm}^{-1}$ ): 1688 ( $\nu(\text{CO})$  amide), 1611 ( $\nu(\text{CO})$

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amide), 1582 ( $\nu(\text{CO})$  amide). ESIMS (negative ion):  $m/z$  557  $[\text{4}]^{-1}$  (100%);  $m/z$  522,  $[\text{4} - \text{Cl}]^{-1}$  (65%).

#### Example 21

5      Synthesis of  $[\text{Ph}_4\text{P}]_5$  [the tetraphenylphosphonium salt of iron(IV) cyano TMDE-DCB monoanion] from  $[\text{Et}_4\text{N}]_4$  [the tetraethylammonium salt of iron(IV) chloro TMDE-DCB monoanion] and NaCN.

10                       $[\text{Et}_4\text{N}]_4$  [the tetraethylammonium salt of iron(IV) chloro TMDE-DCB monoanion] (225 mg, 0.33 mmol) was suspended in  $\text{H}_2\text{O}$  (10 mL). Sodium cyanide (140 mg, 2.85 mmol) was dissolved in  $\text{H}_2\text{O}$  (10 mL) and added to the suspension and the mixture was sonicated (Branson 1200, 0.5h). The purple suspension changed to a deep blue solution and nearly all the solid material dissolved. The mixture was filtered and the blue product was precipitated by adding  $\text{PPh}_4\text{Cl}$  [tetraphenylphosphonium chloride] dissolved in water (600 mg, 1.6 mmol, 10 mL, Aldrich). The blue precipitate was collected and washed with  $\text{H}_2\text{O}$  (2 x 10 mL). Yield: 250 mg (0.28 mmole, ~85%). This material (120 mg) was further purified by thin layer chromatography (TLC) (Silica gel plate, GF, 20 cm x 20 cm x 1000  $\mu\text{m}$ , 10:1  $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{CN}$ ). The blue material was extracted from the silica gel with  $\text{CH}_3\text{CN}:\text{CH}_2\text{Cl}_2$  (1:1, 60 mL). The solvent was removed under reduced pressure and the residue was dissolved in  $\text{CH}_2\text{Cl}_2$  (3 mL) and filtered. Addition of pentane (150 mL) gave a blue powder (90 mg, 0.10 mmol) Yield on purification: (75%). IR (Nujol/NaCl,  $\text{cm}^{-1}$ ): 2129 ( $\nu(\text{CN})$ ), 1659 ( $\nu(\text{CO})$  amide), 1598 ( $\nu(\text{CO})$  amide), 1571 ( $\nu(\text{CO})$  amide). Anal. Calcd for:  $\text{C}_{46}\text{H}_{44}\text{N}_5\text{FeOCl}_2\text{P}$ : C, 62.18; H, 4.99; N, 7.88; Cl, 7.98. Found: C, 61.96; H, 5.04; N, 7.84; Cl, 8.06. ESIMS (negative ion):  $m/z$  548.2,  $[\text{5}]^{-1}$  (100%);  $m/z$  522.1,  $[\text{5-CN}]^{-1}$  (20%). For  $^{13}\text{C}$ -

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labeled cyanide:  $m/z$  549.2,  $[5]^{1-}$  (100%);  $m/z$  522.1,  $[5 - ^{13}\text{CN}]^{1-}$  (8%).

#### Example 22

5 The Synthesis of  $[\text{Ph}_4\text{P}]5$  [the tetraphenylphosphonium salt of iron(IV) cyano TMDE-DCB monoanion] from Nitrile Cyanide Sources.

10  $[\text{Ph}_4\text{P}]5$  [the tetraphenylphosphonium salt of iron(IV) cyano TMDE-DCB monoanion] can be formed in the presence or absence of base. In the absence of base, the blue color fades to yellow-orange as the solvent is removed in the workup procedures. Therefore, product isolation to obtain the blue solid is best carried out in the presence of added base at a pH range of 9-10. The following reaction yields  $[\text{Ph}_4\text{P}]5$  with each of  
15  $\text{CH}_3\text{CN}$ ,  $\text{CD}_3\text{CN}$ ,  $\text{CH}_3\text{CH}_2\text{CN}$  and  $(\text{CH}_3)_2\text{CHCN}$  as the solvent substrates. Base was not added to the catalytic reactions described. It was determined that the blue compound is an effective catalyst precursor by adding isolated  $[\text{Ph}_4\text{P}]5$  to an acetonitrile solution of TBHP  
20 (tertiary butyl hydroperoxide), both the solvent and oxidant were consumed indicating that although  $[\text{Ph}_4\text{P}]5$  is formed as an end product of the catalytic oxidation process it is not a deactivated form of the catalyst.

#### Example 23

25 The Synthesis of  $[\text{Ph}_4\text{P}]5$  in the Presence of Base  
 $[\text{Et}_4\text{N}]3$  (160 mg, 0.23 mmol) was dissolved in the chosen nitrile solvent (6 mL), see Example 19. Tetraethylammonium hydroxide base was added (20 wt %, 0.370 mL, 0.52 mmol, Aldrich), then t-butyl  
30 hydroperoxide (90%, 0.605 mL, 5.4 mmol, Aldrich) was added dropwise with stirring (20 min) resulting in a blue solution. The remaining nitrile was removed under reduced pressure, leaving an oily blue residue which was dissolved in  $\text{H}_2\text{O}$  (15 mL) and filtered. The blue

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material was precipitated from the filtrate by addition of an aqueous solution of  $\text{PPh}_4\text{Cl}$  (800 mg, 2.1 mmol, Aldrich, 10 mL). The blue precipitate was collected and washed with  $\text{H}_2\text{O}$  (2 x 10 mL). Yield: 130, 0.15 mmol (65 %). Further purification was carried out as described in the  $[\text{Ph}_4\text{P}]\text{5}$  section, Example 25.

#### Example 24

X-ray Crystal Structure Data and Refinement for  $[\text{Et}_4\text{N}]\text{3 H}_2\text{O}$

$\text{C}_{29}\text{H}_{48}\text{Cl}_2\text{FeN}_5\text{O}_6$ ,  $M = 689.47$ , Triclinic, Space group P-1,  $a = 9.899(2)$ ;  $b = 11.771(2)$ ;  $c = 14.991(4)$  Å,  $\beta = 95.33(2)^\circ$ ;  $\gamma = 100.09(2)^\circ$ ;  $\gamma = 92.31(2)^\circ$ ,  $V = 1709.6(6)$  Å<sup>3</sup>,  $D_{\text{obs}} = 1.33 \text{ g cm}^{-3}$ ,  $D_{\text{calcd}} (Z = 2) = 1.339 \text{ g cm}^{-3}$ ,  $T = 293 \text{ K}$ ,  $\lambda = 0.71069$  Å,  $\mu = 0.64 \text{ mm}^{-1}$ , trans coeff. 0.87 - 1.00. Diffraction data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer using graphite monochromated Mo-K $\alpha$  radiation. Three reflections were monitored throughout data collection, only random fluctuations in intensity being observed. The structure was solved by direct methods. Hydrogen atoms bonded to the carbon were included in calculated positions with C/H bond distance of 0.96 Å and were refined using a riding model with a thermal parameter 20% greater than the parent carbon. Hydrogen atoms of the water molecule were located from electron density difference maps and their coordinates allowed to refine with the thermal parameter fixed at 20% greater than that of the oxygen. Refinement was by full-matrix least squares on  $F^2$  with scattering factors taken from the International Tables. All non-hydrogen atoms were refined with anisotropic thermal parameters. The final difference maps were featureless. Refinement converged to  $R = 0.053$ ,  $\text{WR2} = 0.112$  with weights  $1.0/[\sigma^2(F_o^2) + \{0.0652 (F_o^2 + 2F_c^2)/3\}^2]$  for 2262 observed reflections.



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Example 25

X-ray Crystal Structure Data and Refinement for [Et<sub>4</sub>N]<sup>4+</sup>

Single crystals of [Et<sub>4</sub>N]<sup>4+</sup> at 20 ± 1 °C are monoclinic, space group P2<sub>1</sub>/c-C<sup>5</sup><sub>2h</sub> (No. 14) with a = 9.958(2) Å, b = 14.956(3) Å, c = 22.688(5) Å, α = 90.00, β = 93.83(2), γ = 90.00, V = 3372(1) Å<sup>3</sup>, and Z = 4 (d<sub>calcd</sub> = 1.357 g cm<sup>-3</sup>; μ<sub>a</sub>(CuKα) = 6.17 mm<sup>-1</sup>). A total of 4626 independent absorption-corrected reflections having 2θ(CuKα) < 115.0° were collected using θ-2θ scans and Ni-filtered CuKα radiation. The structure was solved using "Direct Methods" techniques with the NICOLET SHELXTL software package as modified at Crystalytics Company. The resulting structural parameters have been confined to a convergence of R<sub>1</sub> (unweighted, based on F) = 0.037 for 2680 independent reflections having 2θ(CuKα) < 115.0° and I > 3σ(I). The ten methyl groups were refined as rigid rotors with sp<sup>3</sup>-hybridized geometry and a C - H bond length of 0.96 Å. The initial orientation of each methyl group was determined from difference Fourier positions for the hydrogen atoms. The final orientation of each methyl group was determined by three rotational parameters. The refined positions for the rigid rotor methyl groups have C-C-H angles which ranged from 103° - 118°. The remaining hydrogen atoms were included in the structure factor calculations as idealized atoms (assuming sp<sup>2</sup>- or sp<sup>3</sup>-hybridization of the carbon atoms and a C - H bond length of 0.96 Å) riding on their respective carbon atoms. The isotropic thermal parameter of each hydrogen atom was fixed at 1.2 times the equivalent isotropic thermal parameter of the carbon to which it is covalently bonded.

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Example 26

Lignin Bleaching With Hydrogen Peroxide and Fe-DCB at pH 10

5           Into a 1 cm pathlength quartz cuvette  
containing 3.0 mL of 0.1 M  $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$  (pH 10)  
thermostatted at 25°C was added 60  $\mu\text{L}$  of a saturated  
alkali lignin solution and 300  $\mu\text{L}$  of catalyst stock  
solution ( $1.24 \times 10^{-4}$  M Fe-DCB (wherein R' and R" are  
methyl), all in water. The solution was stirred and  
10   3.8  $\mu\text{L}$  of 30%  $\text{H}_2\text{O}_2$  was added. Absorbance changes at  
350, 376, 400, 426, 450, and 476 nm were measured using  
a Hewlett-Packard UV/Vis spectrophotometer operating in  
the single cell Kinetics mode. Upon addition of the  
 $\text{H}_2\text{O}_2$ , the absorbance increased rapidly at all  
15   wavelengths and then decreased rapidly. After 15 min  
the absorbance at each wavelength was below the  
starting value indicating that lignin bleaching had  
occurred. A second addition of 60  $\mu\text{L}$  of lignin was  
added which caused the absorbances to rise rapidly like  
20   before and then following the initial rise decrease  
more slowly than before. Bubbles formed throughout the  
experiment.

          After 30 mins., an additional 3.8  $\mu\text{L}$  of  $\text{H}_2\text{O}_2$   
was added. The behavior was similar to that observed  
25   previously. A rapid increase in absorbance followed by  
a decay.

Example 27

Lignin Bleaching Without Fe-DCB at pH 10

          The steps of Example 26 were repeated with  
30   the exclusion of the catalyst. Into a 1 cm pathlength  
quartz cuvette containing 3.0 mL of 0.1 M  $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$   
(pH 10) thermostatted at 25°C was added 60  $\mu\text{L}$  of a  
saturated alkali lignin solution and the mixture

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stirred. A short period after data acquisition was initiated, 3.8  $\mu\text{L}$  of 30%  $\text{H}_2\text{O}_2$  was added.

The absorbance measurements were taken using the same parameters as in Example 26.

5           Upon addition of the  $\text{H}_2\text{O}_2$ , all six wavelengths showed a rise in absorbance. The rise was not rapid and did not spike as in the catalyzed reaction. The absorbance gradually began to slope downwards, but did so very slowly. No bubbles were observed in the  
10 mixture within the first 15 min. By the end of the hour, bubbles began to appear.

Comparison of the preliminary experiments in Examples 26 and 27 indicate that the addition of the activator of the present invention increases the rate  
15 at which  $\text{H}_2\text{O}_2$  bleaches lignin.

#### Example 28

Lignin Bleaching With Hydrogen Peroxide, A Sequesterant and No Fe-DCB at pH 10

20           The steps of Example 27 were repeated with the addition of a sequesterant, DEQUEST 2066, 2  $\mu\text{L}$ , a chelating agent for free metal ions. The addition of  $\text{H}_2\text{O}_2$  gave a gradual rise and decay pattern similar to that seen in Example 27.

#### Example 29

25           Lignin Bleaching With Hydrogen Peroxide, A Sequesterant and no Fe-DCB at pH 7

30           The steps of Example 27 were repeated at pH 7 using a 0.0087 molal  $\text{KH}_2\text{PO}_4$ /0.030 molal  $\text{Na}_2\text{HPO}_4$  buffer. 2  $\mu\text{L}$  DEQUEST 2066 chelating agent was added to the cuvette. No discernible bleaching occurred within the 1 hr time-frame of the experiment. Minimal activity was observed in the 350nm absorbance trace, but was attributed to noise.

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Example 30

Lignin Bleaching With Hydrogen Peroxide, Fe-DCB and A Sequesterant at pH 10

5 Into a cuvette equipped with a stir bar,  
1 equivalent of the catalyst of Example 26 (300  $\mu$ L  
stock solution of Fe-DCB), 60  $\mu$ L saturated lignin  
solution buffered as before and 2  $\mu$ L DEQUEST chelating  
agent were mixed. Absorbance was measured using the  
same parameters as described in Examples 26 and 27.

10 After 1-2 min., 1000 equivalents 30%  $H_2O_2$  (3.8  
 $\mu$ L) was added to the cuvette. This caused the rapid  
rise in absorbance followed by rapid decrease as  
described in Example 26.

15 After 20 min., an additional 60  $\mu$ L lignin was  
added to the cuvette. The absorbance at all  
wavelengths rose more slowly and then decayed more  
slowly than following the addition of the  $H_2O_2$ .

20 After 30 min., an additional equivalent (300  
 $\mu$ L) of catalyst (Fe-DCB) was added. No significant  
changes were observed.

After 40 min., an additional 3.8  $\mu$ L  $H_2O_2$  was  
added to the cuvette. This caused a significant  
decrease in the absorbance at all wavelengths  
indicating that lignin bleaching was again occurring.

25 Example 31

Lignin Bleaching With Hydrogen Peroxide, Fe-DCB, and A  
Sequesterant at pH 7 absorbance should be changed to  
absorbance.

30 Example 29 was repeated but with the addition  
of 300  $\mu$ L catalyst. 3.8  $\mu$ L 30%  $H_2O_2$  was added after a  
few cycles. Upon the addition of  $H_2O_2$ , the absorbances  
rose at each of the six wavelengths used in Example 26,  
but not dramatically. The absorbances continued to  
rise slowly for the first 15 min., plateaued, and then

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began to fall for all six wavelengths. After one hour, the absorbances were higher than the initial absorbance.

#### Example 32

##### 5 Sustained Catalyst Activity

Into a 1 cm pathlength quartz cuvette containing 3.0 mL of 0.1 M  $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$  (pH 10) thermostatted at 25°C was added 60  $\mu\text{L}$  of a saturated alkali lignin solution, 300  $\mu\text{L}$  (12.4  $\mu\text{M}$ ) of catalyst stock solution ( $1.24 \times 10^{-4}\text{M}$  Fe-DCB), and 2  $\mu\text{L}$  Dequest 10 2066 all in water. The mixture was stirred, data acquisition was initiated as in Example 26, and then 19  $\mu\text{L}$  (5000 equivalents) of 30%  $\text{H}_2\text{O}_2$  was added. After the first rapid rise in absorbance followed by rapid decay, 15 aliquots of 60  $\mu\text{L}$  saturated alkali lignin solution and 19  $\mu\text{L}$  (5000 equivalents) of 30%  $\text{H}_2\text{O}_2$  were added every 15 min.

The results obtained at the 476 nm monitored wavelength are shown by the solid line in the graph of Fig. 1. Similar results were obtained at the other 20 wavelengths monitored. Additions of lignin and  $\text{H}_2\text{O}_2$  are shown by asterisks.

For comparison, a cuvette of the saturated solution of lignin, chelating agent and  $\text{H}_2\text{O}_2$  without 25 catalyst was prepared and the absorbance measured. The results are shown by the dashed line in Fig. 1.

#### Example 33

##### Sustained Catalyst Stability

With reference to Fig. 5, the catalytic 30 longevity of two embodiments of the invention were compared in a dye test. Compound 1 had substituents  $\text{R}'$  and  $\text{R}''$  each as  $\text{CH}_3$ , while Compound 2 had substituents  $\text{R}'$  and  $\text{R}''$  each as  $-\text{CH}_2\text{CH}_3$ . The control was no catalyst added.

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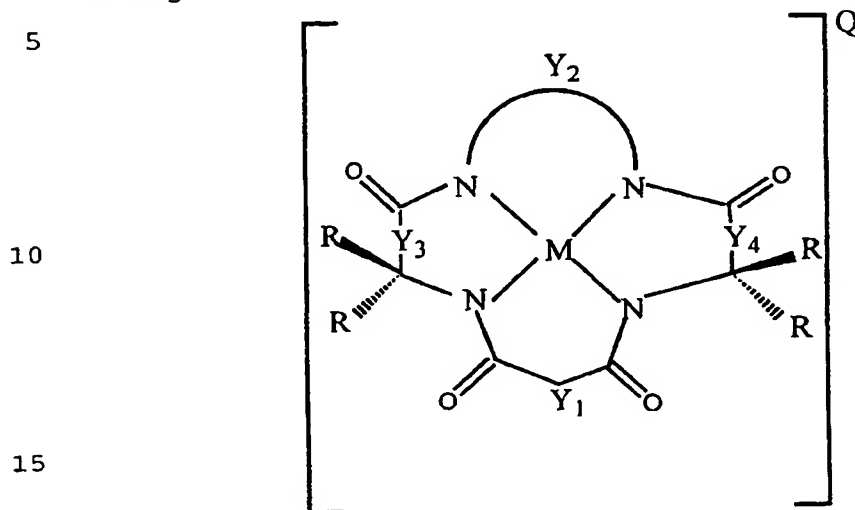
The conditions were pH 9, room temperature (21.1°C), with a buffer system of  $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ . Oxidant was 4mM (30%)  $\text{H}_2\text{O}_2$ . At each of the asterisks, 12  $\mu\text{M}$  pinacyanol chloride dye was added.

5           As can be seen from the graph in Fig. 5, each addition of dye where Compound 1 was present resulted in almost immediate decolorization. Compound 2, the diethyl compound, had more gradual decolorization. The control showed only a very gradual rate of  
10 decolorization.

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CLAIMS

1. A bleaching composition comprising:  
 (a) an oxidatively stable bleach activator  
 having the structure



wherein  $Y_1$ ,  $Y_3$  and  $Y_4$  each represents a bridging group having zero, one, two or three carbon containing nodes for substitution, and  $Y_2$  is a bridging group having at least one carbon containing node for substitution, each said node containing a  $C(R)$ ,  $C(R_1)(R_2)$ , or a  $C(R)_2$  unit and each R substituent is the same or different from the remaining R substituents and is selected from the

25 group consisting of H, alkyl, cycloalkyl, cycloalkenyl, aryl, alkynyl, alkylaryl, halogen, alkoxy, or phenoxy,  $CH_2CF_3$ ,  $CF_3$  and combinations thereof, or form a substituted or unsubstituted benzene ring of which two carbon atoms in the ring form nodes in the Y unit, or

30 together with a paired R substituent bound to the same carbon atom form a cycloalkyl or cycloalkenyl ring, which may include an atom other than carbon; M is a transition metal with oxidation states of I, II, III, IV, V, VI, VII or VIII or selected from Groups 6, 7, 8,

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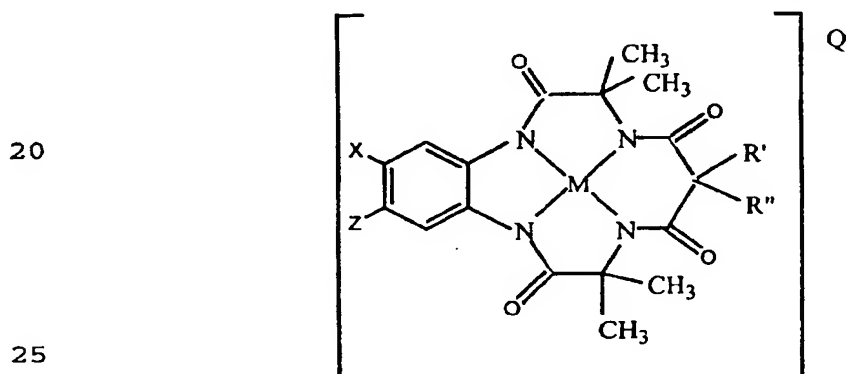
9, 10 and 11 of the Periodic Table of the Elements; and Q is any counterion which would balance the charge of the compound on a stoichiometric basis; and

(b) an effective amount of a source of an  
5 oxidant.

2. The bleaching composition of claim 1 wherein said oxidant is a peroxy compound.

3. The bleaching composition of claim 1 wherein said peroxy compound is selected from the group  
10 consisting of hydrogen peroxide, hydrogen peroxide adducts, compounds capable of producing hydrogen peroxide in aqueous solution, organic peroxides, persulfates, perphosphates, and persilicates.

4. The bleaching composition of claim 1  
15 wherein the oxidatively stable bleach activator is a macrocyclic tetraamido ligand having the structure:



wherein X and Z may be H, electron donating or electron-withdrawing groups and R' and R'' may be any combination of H, alkyl, cycloalkyl, cycloalkenyl, alkenyl, aryl, alkynyl, alkylaryl, halogen, alkoxy, or  
30 phenoxy substituents, or combine to form a cycloalkyl or cycloalkenyl ring, which may contain at least one atom that is not carbon; M is a transition metal with oxidation states of I, II, III, IV, V, VI, VII or VIII or selected from Groups 6, 7, 8, 9, 10 and 11 of the



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Periodic Table of the Elements; Q is any counterion which would balance the charge of the compound on a stoichiometric basis.

5           5. The bleaching composition of claim 4 wherein X and Z are independently selected from the group consisting of H, halogen, SO<sub>3</sub>, OSO<sub>3</sub>, OSO<sub>3</sub>R (wherein R is H, alkyl, aryl, or alkylaryl) and NO<sub>2</sub>.

          6. The bleaching composition of claim 4 wherein R' and R" are selected from H and C<sub>1-6</sub> alkyl.

10           7. The bleaching composition of claim 1 further comprising a further adjunct selected from the group consisting of sequesterants and cellulose-based material bleaching adjuncts.

          8. The bleaching composition of claim 4 wherein M is Fe or Mn.

          9. The bleaching composition claim 4 wherein R' and R" are selected from C<sub>1-6</sub> alkyl, or join together to form a cycloalkyl or cycloalkenyl, optionally with at least one atom which is not carbon.

20           10. The bleaching composition of claim 3 wherein X and Z are H.

          11. The bleaching composition of claim 1 further comprising a ligand L bound to the metal M.

25           12. A method of bleaching comprising contacting cellulose-based materials with the composition of claim 1.

          13. The method recited in claim 12 wherein the oxidant is a peroxy compound.

30           14. The method recited in claim 13 wherein the peroxy compound is hydrogen peroxide.

          15. The method recited in claim 13 wherein the temperature is within the range of ambient to about 80 °C.

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16. The method recited in claim 13 wherein the temperature is within the range of ambient to about 40 °C.

5 17. The method recited in claim 13 wherein the pH is within the range of 7 and 11.

18. A method of bleaching comprising contacting cellulose-based materials with the composition of claim 3.

10 19. The method recited in claim 18 wherein the cellulose-based material is wood pulp.

20. A method of oxidizing lignin comprising contacting lignin in solution with the composition of claim 1.

15 21. A method of bleaching lignin comprising contacting lignin with the composition of claim 1.

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Reaction conditions:

Catalyst:  $[\text{Fe}(\text{DCB}^*)(\text{H}_2\text{O})]^-$ Oxidant: 5000 equiv.  $\text{H}_2\text{O}_2$ T:  $25^\circ\text{C}$ pH: 10 (0.1 M  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ )

Sequesterant: Dequest 2066

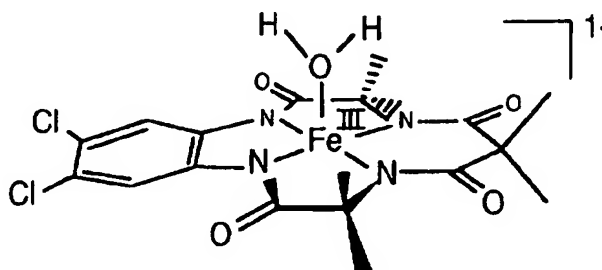
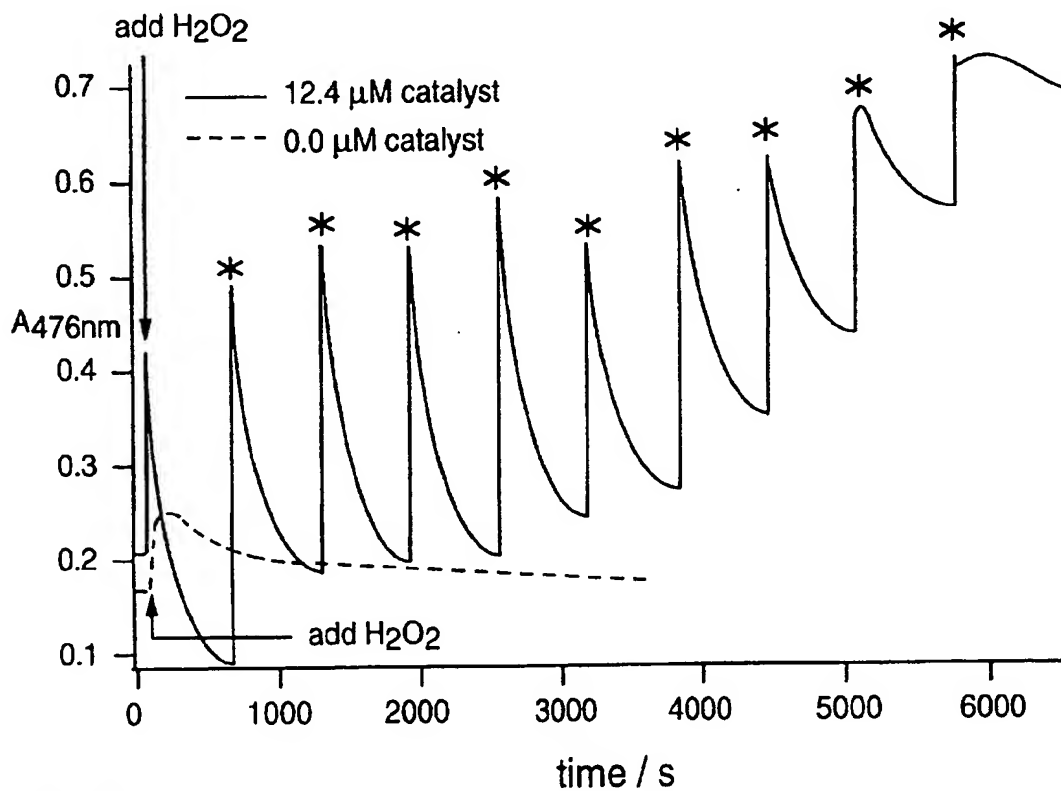
\* = add 60  $\mu\text{L}$  of saturated solution of alkali lignin and  $\text{H}_2\text{O}_2$  (5000 equiv)

FIG. 1

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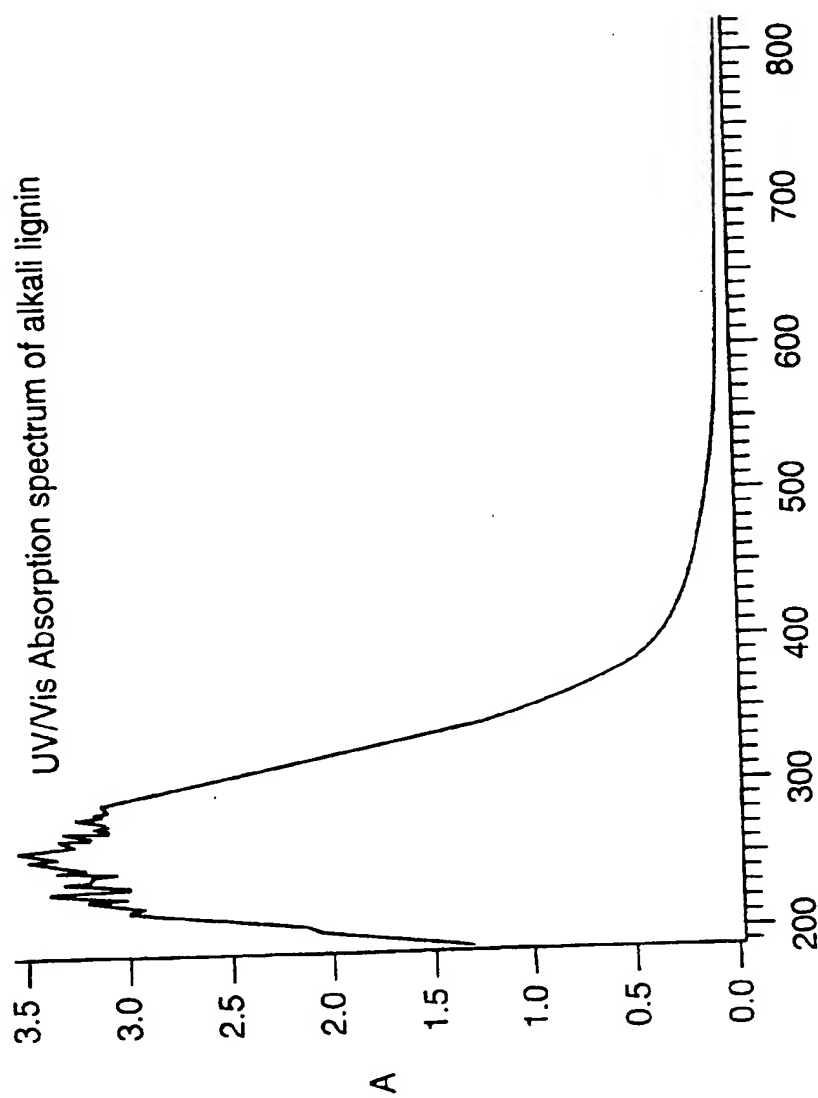


FIG. 2

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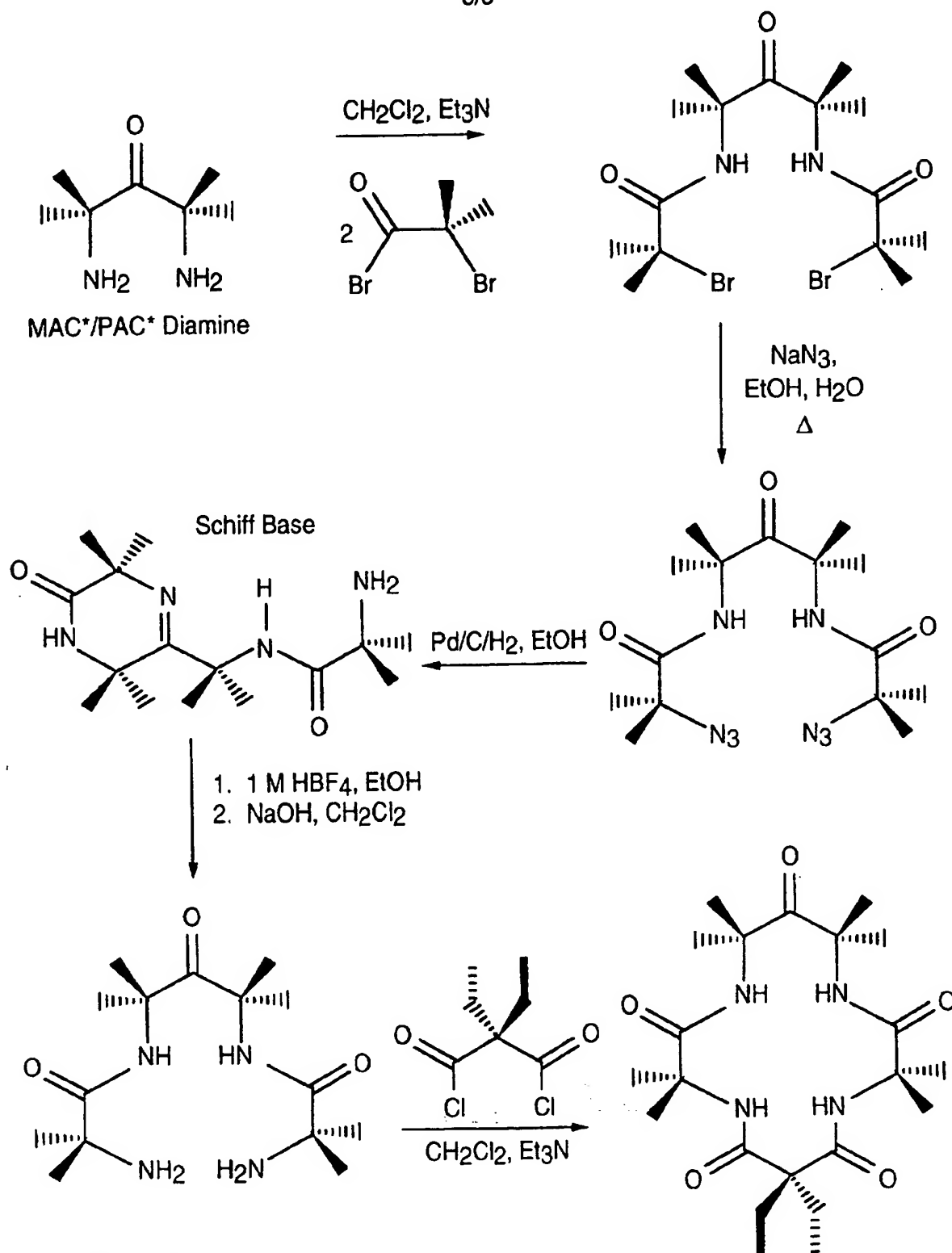


FIG. 3

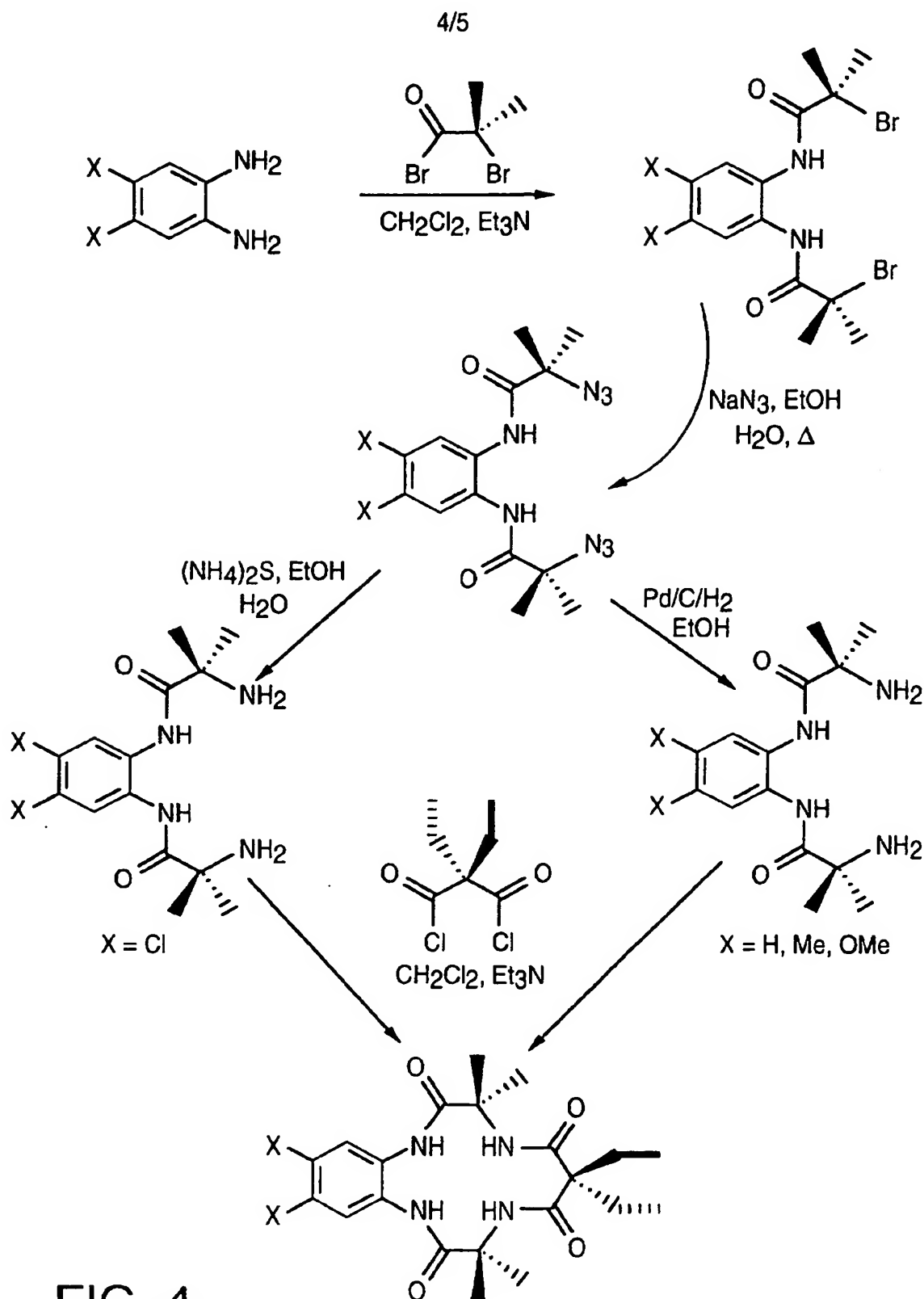


FIG. 4

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Catalyst:  
 0.4 mM  $[\text{Fe}(\text{H}_2\text{O})\text{DCB}^+]$  -  
 0.4 mM  $[\text{Fe}(\text{H}_2\text{O})\text{DCB}]^-$   
 0.0 mM catalyst  
 12  $\mu\text{M}$  pinacyanol chloride dye  
 4 mM 30%  $\text{H}_2\text{O}_2$  oxidant  
 pH ~ 9  $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$

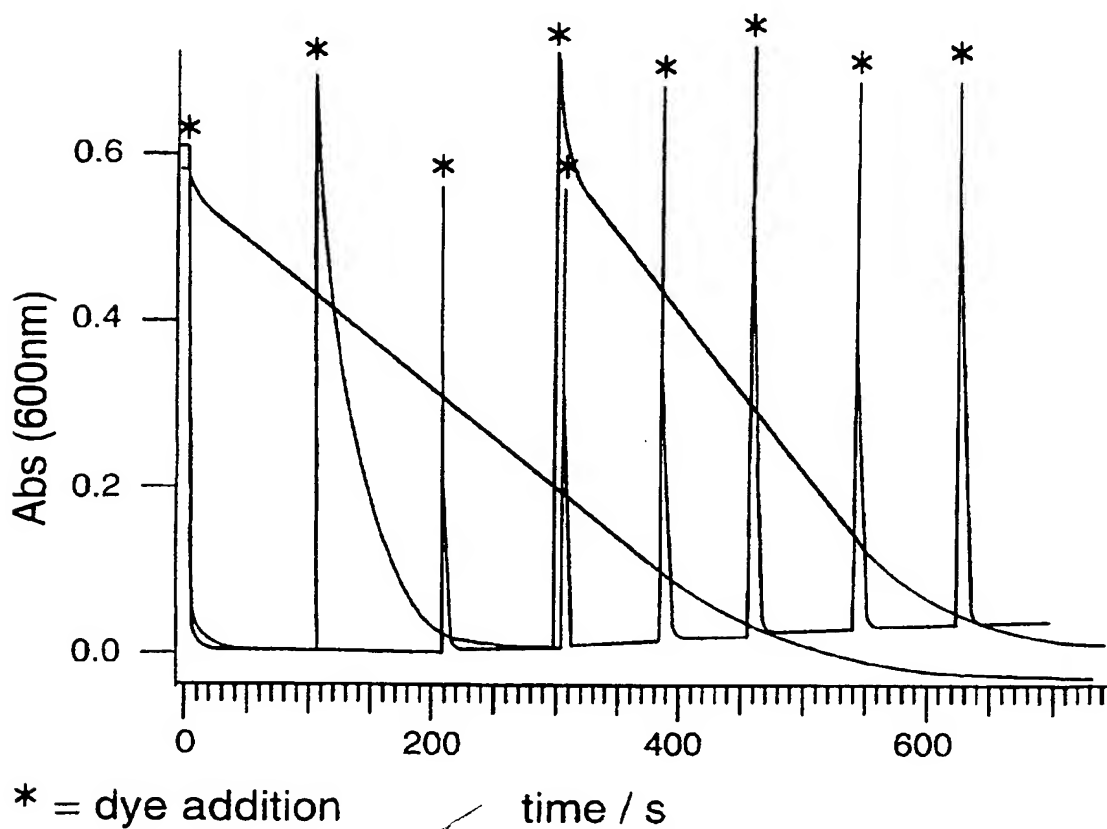
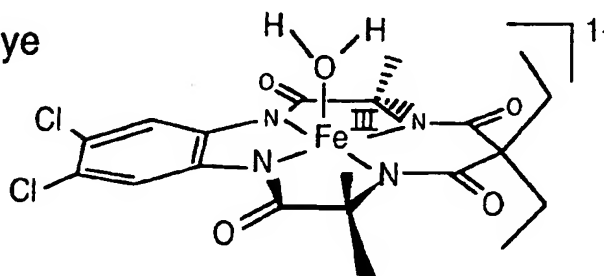
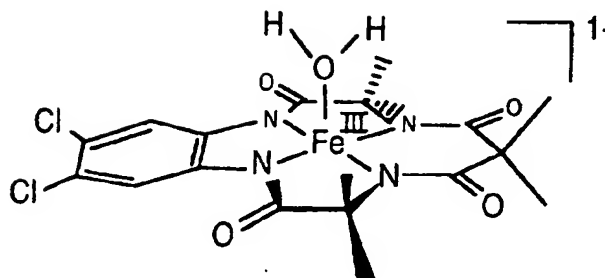


FIG. 5